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Y3.N88:25/2333/v.2

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NUREG/CR-2333
BNL-NUREG-51458
Vol. 2

ORIGINAL

Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC

Task 2
Alternative TRU Technologies

Prepared by G. Bida, D. R. MacKenzie

Brookhaven National Laboratory

Prepared for
U.S. Nuclear Regulatory Commission

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II

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Task 2
Alternative TRU Technologies

Manuscript Completed: September 1981
Date Published: February 1982

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Division of Waste Management
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NRC FIN A3158

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All references made to the BNL interim reports, "NRC Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria," Tasks 1-5, should be disregarded. The following references should be inserted in their places, as applicable.

R. Dayal, et al., "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 1: Waste Package Overview," NUREG/CR-2333, Vol. 1, BNL-NUREG-51458, February 1982.

G. Bida, et al., "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 2: Alternative TRU Technologies," NUREG/CR-2333, Vol. 2, BNL-NUREG-51458, February 1982.

D. Majumdar, et al., "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 3: Waste Inventory Review," NUREG/CR-2333, Vol. 3, BNL-NUREG-51458, February 1982.

T.M. Ahn, et al., "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 4: Test Development Review," NUREG/CR-2333, Vol. 4, BNL-NUREG-51458, February 1982.

M.S. Davis, "Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC, Task 5: National Waste Package Program," NUREG/CR-2333, Vol. 5, BNL-NUREG-51458, February 1982.

ABSTRACT

Three main areas of transuranic (TRU) waste management are addressed: immobilization processes and waste forms for ultimate geologic disposal of TRU waste; decontamination as a method for TRU waste management; and potential problems associated with gas generation by certain TRU wastes. Waste forms are considered in terms of the regulations and criteria proposed in 10 CFR 60. Evaluation of the waste forms is based principally on ability to meet the release rate criterion of 10^{-5}/year given in the Performance Objectives of Section 111, but also on the general requirements of Section 133. The two classes of metallic waste which are candidates for decontamination treatment are Zircaloy cladding hulls from light water reactor fuel elements, and failed facilities and equipment. Decontamination methods are addressed with regard to their ability to remove contamination to a level below the 10 nCi/g TRU limit. Other important factors are the volume reduction achieved, and compatibility of the secondary waste streams with acceptable waste forms. Gas generation by combustible TRU wastes and cast concretes containing TRU isotopes is discussed, and its potential for damage to a geologic repository is considered. Exclusion of combustible TRU waste from repositories is recommended. Conclusions are drawn about the suitability of various waste forms and recommendations are made regarding further work needed in the development of specific TRU waste forms.

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ACKNOWLEDGMENTS

The authors are indebted to K. J. Swyler for writing Section 2.9 on the effects of radiation on proposed TRU waste forms. We greatly value the useful and informative discussions we have had with the personnel of TWSO and numerous other scientists and engineers in the DOE community, particularly those involved in the TRU waste management area.

The cheerful and untiring efforts of Grace Searles and Sharon Moore in preparing the manuscript are most gratefully acknowledged.

EXECUTIVE SUMMARY

This final report contains an assessment of certain transuranic (TRU) waste management technologies. The evaluation results from a review of, primarily, relevant DOE research and development efforts, although some foreign work has also been included. The topical reports, progress reports, and contributions to scientific and technical meetings reviewed to date, cover work done up to the end of CY 80. The three specific areas of interest to NRC which are addressed in this report are alternate TRU waste forms for ultimate geologic disposal, management of TRU waste by decontamination, and the potential for gas generation of TRU-bearing waste. The objectives of the report are (1) to provide NRC with the information necessary for the licensed geologic disposal of commercial TRU waste, (2) to recommend appropriate courses of action that provide support for proposed regulations and criteria and lead to the safe isolation of commercial TRU waste, and (3) to identify research needed to reduce significant uncertainties.

The first part of this report reviews TRU waste forms in terms of their ability to meet the controlled radionuclide release rate criterion that the proposed NRC rule (10 CFR 60) places on the engineered system. This approach was requested by NRC so that TRU waste forms could be evaluated as creditable engineered barriers. It is important to note that the maximum radionuclide release rate criterion applies to the total inventory of waste in the repository. Thus, the total inventory of actinides includes the actinides in high level waste as well as those in TRU waste. It should be emphasized again, however, that the proposed rule places the controlled release rate criterion on the engineered system, not on the waste form. Thus, the Applicant, in demonstrating that the engineered system meets the maximum release rate criterion (i.e., 1×10^{-5}/year) for the total actinide inventory, can take full credit, partial credit, or no credit for the TRU waste form. A condensed version of the major conclusions is presented below.

In addition to being conclusions, some of these points indicate areas that are obviously in need of additional effort if these waste forms are to meet the actinide release rate criterion of 10^{-5}/yr.

- An insufficient data base exists for all the TRU waste forms reviewed.
- In terms of the 10^{-5}/yr actinide release rate criterion, no TRU waste form under development has been shown to meet this requirement with any degree of confidence. In fact, the dearth of available information on the waste forms discussed leads us to conclude, at this time, that no credit can be taken by DOE for the waste form as an engineered barrier.
- In some cases, the TRU waste stream has not been adequately characterized.
- Few data are reported for waste forms containing actual waste.
- Inadequate information exists for the sensitivity of waste form properties to physical and chemical variations in the waste.

- Outside of the comparative assessment study at PNL, no standard test methods have been used in the evaluation of material properties.

- As concerns radiation damage, the available evidence indicates that effects due to alpha particle and recoil nucleus events are not expected to be a determining factor. However, this cannot be confirmed until the ranges of waste form composition and loadings are specified.

- The combination of certain TRU waste streams, e.g., incinerator ash and process sludges, with a HLW stream for processing into a single waste form appears to be a technically feasible strategy based on the available data.

Decontamination of non-combustible TRU waste has the potential to reduce considerably the volume requiring disposal in a geologic repository. For this potential to be realized, the secondary waste stream of removed TRU contamination not only must be much smaller than the original waste volume, but also must be compatible with an acceptable waste form. These conditions can be met by most of the decontamination methods reviewed, all of which have been developed, at least on a laboratory scale, to the stage where equipment can be decontaminated to below the 10 nCi/g level (which defines TRU waste), and thus be classed as non-TRU waste suitable for shallow land burial.

Potentially hazardous gaseous mixtures can be produced by degradation of TRU contaminated organic material contained in its original form, and radiolysis of the matrix used to immobilize TRU waste streams such as incinerator ash and process sludges. The major degradation mechanisms discussed are microbial, thermal, and radiolytic. Of these, microbial degradation can potentially produce larger quantities of gas than the other two. Because of disagreements and uncertainties in the existing data, rates of gas generation and quantities produced are in question. Depending on the choice of waste forms, gas generation from degradation can be eliminated or greatly reduced by processing the combustible waste, followed by immobilization of the residue in a suitable waste form.

Based on our review of the available literature up to the end of approximately CY 80 and the nature of the evaluation conducted for TRU waste forms, we have made several recommendations (listed below) for NRC consideration.

1. It is recommended that combustible organic TRU waste not be allowed in licensed repositories. Such material almost certainly will not meet a numerical performance criterion such as that adopted for the purpose of this report. Even in lieu of such a release rate criterion, no credit can be given to the as-generated TRU inventory as a major engineered barrier. Since processing techniques are well established (e.g., incineration and acid digestion), it seems reasonable to require that all organic waste be processed and the residue immobilized in a suitable waste form for repository emplacement. Further support for this position is obtained from volume reduction considerations plus ease of regulatory compliance for purposes of handling, transportation, and mine emplacement.

2. In view of the major advantages associated with volume reduction, which are achieved by decontaminating metallic waste, and since a range of well developed decontamination methods are available, it is recommended that removal of TRU contamination from metals be considered as the preferred disposal method for licensed geologic repositories. Research recommendations include: (a) continuation of the development work necessary to demonstrate, on an engineering scale, a method (or methods) for decontamination of LWR cladding hulls and (b) demonstration that the secondary waste stream from electropolishing can be kept small and suitable for incorporation in a satisfactory TRU waste form.

3. In terms of process simplification, demonstration of technical feasibility, and decreased risk to the public, there is merit to the idea of combining HLW and TRU waste. It is recommended that combined processing of both waste streams be pursued in all appropriate situations, such as when technical feasibility can be shown and when both HLW and TRU waste are generated at the same site.

4. The waste form-specific recommendations are too numerous and lengthy to be listed in this summary. Instead, some generic recommendations are listed below.

   - We recommend that the following waste forms be excluded from any further serious consideration as alternative TRU waste forms: (1) the existing TRU waste inventory, (2) Urea-formaldehyde resin, (3) Bitumen, and (4) Normal cast concrete.

   - The extent of the solubility of various actinides in glassy and crystalline phases appears to be well known only for borosilicate glass and monazite. Solubility limits should be determined for the other candidate TRU waste forms discussed in this report.

   - Data on the phase characterization and actinide partitioning in the candidate waste forms are either scarce, incomplete, or lacking altogether. In the final analysis, these data must be obtained for production prototypic radioactive waste forms. The phases identified for lab-scale samples may not necessarily be representative of those present in large scale products.

   - The role of various waste stream constituents in the formation of a durable product should be elucidated, for example, that of iron in Iron-Enriched Synthetic Basalt.

   - In the area of radiation stability:

     1. an improved understanding of the metamict state, and the metamict "transition", would increase our confidence in the isolation capabilities of crystalline TRU waste forms. Some effort should be directed toward investigating dose rate effects and establishing the degree of equivalence between the metamict state in natural analogues and laboratory samples. Certainly, the effect of metamictization on leach behavior should be unambiguously determined.

2. The possibility of increased radiation damage susceptibility due to alteration under the repository environment (e.g., by incongruent leaching) should be evaluated.

- There is an obvious need for actinide leach data. In this area, we recommend:

  1. use of standardized (MCC) tests with actual waste loaded samples,

  2. use of waters equilibrated with repository rock and/or potential geologic environments,

  3. that the leach mechanisms for the various waste forms be understood for long term predictive capability,

  4. thorough investigation of the possibility that actinide leach rates are solubility limited at low groundwater flow rates, and

  5. if such is the case, then the concept of valence state control of the actinides in the candidate waste form should be pursued.

1. INTRODUCTION

1.1 Historical Background

Transuranic (TRU) waste is made up of materials which contain or are contaminated by transuranic elements. These elements characteristically emit alpha particles and have half-lives measured in thousands of years. Alpha particle radiation requires little shielding for biological protection but alpha emitters are dangerous if ingested or inhaled. Primary concern comes from the long lifetimes during which they remain radioactive.

Early practice allowed disposal of TRU waste by shallow land burial because the threat to health and safety was perceived as being small. Concern over long times required for containment and experiences with some leakage and migration resulted in a determination by AEC in 1970 that TRU wastes should not be placed in shallow land burial sites. At that time, it was decided that all waste containing more than 10 nCi/g of transuranics would be classified as TRU waste and stored retrievably. Recently, the Environmental Protection Agency (EPA) has proposed setting the TRU limit at 100 nCi/g,[1] but the official figure is still 10 nCi/g. TRU waste storage has been primarily at the Idaho National Engineering Laboratory (INEL), the Rockwell Hanford Operation (RHO), the Los Alamos Scientific Laboratory (LASL), and the Savannah River Plant (SRP). Of the 54,000 m^3 presently stored,[2] about 75% (v/v) is at INEL. Before retrievable storage was begun, many times this amount had been generated and buried, the greater part of it from the defense program,[3] which alone has contributed more than 300,000 m^3. These amounts indicate the magnitude of the problem faced in the management of this type of waste.

Since TRU waste is not permitted in shallow land burial sites, its ultimate disposal will be in mined geologic repositories of the same type as proposed for high level waste (HLW). Originally it was planned that NRC would license all such repositories, and the HLW and TRU waste to be placed in them. Proposed technical criteria for regulating geologic disposal of high level radioactive waste were published as 10 CFR Part 60 in the Federal Register in May 1980.[4]*

NRC's proposed technical criteria for regulating geologic disposal of high level radioactive waste and TRU waste (10 CFR 60) has changed from the draft version used for our Interim Report to the version published in the Federal Register.[4] The principal change in the Repository Performance Objectives (Section 60.111) is one of emphasis on the parts of the repository which must provide reasonable assurance of meeting the criterion of one part in 10^5 annual radionuclide release rate. The earlier version placed this criterion on the waste package alone whereas the recent Federal Register version places it on the engineered system. The engineered system is defined in 10 CFR 60 to include the waste package and an underground facility.

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*The proposed rule (published in the Federal Register July 8, 1981) includes some changes from the May 13, 1980 draft which was referenced during preparation of the report. Changes were made in the definition of the waste package and in the statement of performance objectives as well as in other areas.

BNL's task on alternative TRU technologies includes review and evaluation of the methods proposed for processing TRU waste into suitable forms for geologic disposal, in the light of the above criteria and regulations. The task is divided into three areas:

- Waste forms
- Management of TRU-containing wastes
- Gas generation

Although these subtasks are interrelated, they are sufficiently independent that they may be discussed in separate sections of this report.

At present, since essentially no existing TRU waste is subject to NRC regulation, our evaluation of DOE TRU waste programs could perhaps be considered to be of limited use. However, since there is a fairly high probability that reprocessing of fuel from commercial reactors will be started before long, and since TRU waste from commercial sources will be under NRC jurisdiction, such an evaluation will certainly be useful at that time. The objective of this report is to provide NRC with information necessary for the licensed geologic disposal of TRU waste.

1.2 References

1. R. E. Christensen and N. E. Miller, Battelle Memorial Institute, "Acceptance Criteria for Transuranic Waste Packages for Disposal in a Licensed Geologic Repository," BMI-X-702, September 1980.[a]

2. U. S. Department of Energy, "Spent Fuel and Waste Inventories and Projections," ORO-778, August 1980.[a]

3. A. F. Perge and V. G. Trice, Jr., "Management of Transuranium-Contaminated Solid Waste From the Department of Energy Nuclear Materials Production R&D Programs," Proceedings, NEA/IAEA Technical Seminar on Treatment, Conditioning, and Storage of Solid Alpha-Bearing Waste and Cladding Hulls, Paris, France, December 1977.[b]

4. U. S. Nuclear Regulatory Commission, "10 CFR Part 60: Technical Criteria for Regulating Geologic Disposal of High-Level Radioactive Waste," Federal Register, Vol. 45, No. 94, May 13, 1980, pp. 31393-31408.[b]

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[a]Available for purchase from the National Technical Information Service, Springfield, VA 22161.
[b]Available in public technical libraries.

2. WASTE FORMS

2.1 General Considerations

2.1.1 NRC Requirements

The general requirements for the waste package and the overall engineered system as set out in the Performance Objectives of 10 CFR 60[1] have been discussed in the Introduction to this Report (Section 1.1). For TRU wastes 1000-year containment is of no advantage because of the long lived TRU radioisotopes, and Section 60.111(c)(3)(ii) considers that their release rates must be controlled from the time of decommissioning rather than starting 1000 years after decommissioning, as in the case of HLW. Thus, for TRU waste, the container of the waste package is not required to be a barrier to radionuclide migration, and need only meet the condition that the waste be retrievable for a period of 50 years after completion of emplacement, presumably in intact condition. In fact, the waste form itself is not necessarily required to be a barrier --the only mention of TRU waste is in the release rate section [60.111(c)(3)] which specifies that the engineered system provide reasonable assurance of, at most, one part in 10^5 annual release rate.

Our task is to evaluate waste forms, and it should be carried out in terms of NRC regulations (or proposed regulations) as contained in 10 CFR 60. However, we have chosen to use the one part in 10^5 annual release rate as the principal basis on which to do the waste forms evaluation. We also consider in the evaluation, but to a lesser extent, the Waste Form Requirements [Section 133(b) of 10 CFR 60] which deal with prohibition of liquids, respirable fines, explosive, pyrophoric and toxic materials, and combustibles. The last two topics are taken up in more detail in Section 4 of this report.

The rationale for using the annual release rate criterion as the principal basis for our evaluation is as follows. Since the rate (10^{-5}/yr) is specified for the engineered system as a whole, the Department of Energy (DOE) can attempt to show a repository meets licensing criteria by developing any one barrier to the point where it alone meets the requirements, or by using any combination of barriers to do the same thing. In other words, if DOE can show that the waste form or the backfill or any other barrier can meet the 10^{-5}/yr release rate by itself, any help obtained from the other barriers is a bonus. Thus, our choice of evaluating waste forms based on an upper release rate limit of 10^{-5}/yr represents a conservative approach to system design requiring that each of the components meet or exceed proposed standards. Furthermore, single component testing of candidate components is a more manageable strategy since individual component performance can be evaluated relatively rapidly. Similarly, DOE can get credit for whatever release rate a given barrier achieves, to contribute to the overall engineered system performance. Thus, we evaluate DOE waste forms not merely on whether or not they appear able to achieve the required overall release rate for the repository, but also in terms of how much credit they can be given towards meeting the overall rate.

NRC's Task 2 Statement of Work (SOW) requests BNL to evaluate techniques for TRU waste treatment that "...produce waste forms providing the lowest release rates reasonably achievable" and gives no numerical value while the

present version of 10 CFR 60 still calls for assurance that "...TRU waste will be released at a rate that is as low as reasonably achievable," [Section 60.111(c)(3)(ii)], but then specifies the maximum permissible rate of 10^{-5}/yr already discussed. Thus, we consider that our choice of this release rate, rather than the "as low as reasonably achievable (ALARA)" rate as the basis for our evaluation, is tenable, particularly since the ALARA considerations provide no firm quantitative foundation for an evaluation.

2.1.2 Thermal and Radiation Conditions

Section 60.133(a) of 10 CFR 60 requires DOE to "provide reasonable assurance that the in situ chemical, physical, and/or nuclear properties of the waste package and/or its interactions with the emplacement environment will not compromise the function of..." the waste package itself, or the engineered elements of the geologic repository. Of the factors to be considered in supporting analyses, thermal loads, radiolysis, and radiation damage are the more important external conditions, particularly for HLW. Unless HLW and TRU are disposed of in the same repository, the thermal and radiation fields, particularly the thermal, will be much lower for the TRU waste. If both types of waste are emplaced in the same repository, DOE conceptual repository designs suggest that they will be located on different levels and some distance apart.[2] In this case, any increase in thermal and radiation fields affecting the TRU waste will be relatively small.

The possible effects of HLW on TRU waste when both are in the same repository are discussed in Section 5.4.2. Assuming TRU waste and HLW are not in the same repository, the TRU waste form temperature will be relatively low, with the temperature at the container surface expected conservatively to be no more than 30-40°C.[2] The ionization density caused, per curie, by alpha-radiation from TRU isotopes, is considerably greater than that of the beta, gamma-radiation from fission product isotopes. However, total energy deposition in TRU waste will be much lower because of the much lower total number of curies. Even though the total dose and the dose rate to TRU waste will be much lower than to HLW, radiation damage to the TRU waste form is a potential problem, particularly as it could affect leach rates. This subject is discussed for the different waste forms where information is available.

2.1.3 Conventional TRU Waste Forms

Much of the work on waste forms specifically applied to TRU waste has been based on rather simple concepts. A number have involved mixing solid TRU waste (including organics) in a steel drum with a liquid or slurry, such as bitumen, urea-formaldehyde resin or concrete, and letting the mixture set. The much more complex systems, borosilicate glasses, have been extensively studied as HLW forms, and processes for fabricating TRU waste forms of borosilicate glass have been undergoing development in this country. These forms will be described and evaluated in the following sections.

Another type of TRU waste which we class under the heading of "Conventional TRU Waste Forms" is containerized combustible and non-combustible trash. Although perhaps not a waste form in the conventional meaning of the term, it probably must be considered as one by virtue of being that portion of the waste package which is placed inside a container before emplacement in the geologic repository. Available information on leach rates from this type of waste is discussed in Section 2.2, along with DOE's rationale for using this method of disposing of defense TRU waste.

2.1.4 Waste Forms Based on Natural Minerals and Other Alternatives

Several forms on the level of sophistication of borosilicate glass have been suggested, or are being developed, for TRU waste. Others which are being considered for HLW would be equally suitable for TRU. The latter include porous glass and coated ceramics. In the first category are forms based on natural mineral phases such as monazite, basalt, and SYNROC. Work on monazite has been carried out in several places in the U. S. Use of SYNROC specifically as a TRU waste form is not under investigation yet, but actinide oxides and other waste constituents are readily incorporated into the host lattices of its mineral phases. Work on basalt glass ceramic as a TRU waste form has been under development at Idaho National Engineering Laboratory (INEL) and Pacific Northwest Laboratory (PNL).

2.2 TRU Waste as an Engineered Barrier

In DOE's evaluation of salt beds for TRU waste disposal, the major barrier to radionuclide migration is considered to be the local geomedium. It is anticipated that isolation will be provided by large thicknesses of low permeability salt, a favorable hydrology near the site, and by the sorption properties of the surrounding rock salt and other rocks.[3] Bounding consequence assessment calculations have been made for several radionuclide release scenarios.[2] These analyses examined radionuclide transport through the surrounding geologic media and then through the biosphere. The amounts of radionuclides that might reach people along different pathways were estimated and used to calculate the radiation doses that might result from the assumed releases. The site-specific analyses used detailed geologic and hydrologic models of the area around the site. This included empirical data for both the flow system and the sorptive capacity of the rock.

An additional important assumption for the consequence assessment regarding the physical and chemical condition of the waste was that the radionuclides dissolve at the same rate as the salt when water comes into contact with the waste. It was further assumed that the radionuclides are uniformly mixed with the backfill material at the time of release. The reason for the waste leachability assumption is simple--no leach rate data have been obtained for the existing TRU waste. It has been recognized that leaching studies on existing waste forms would be experimentally difficult because of the large variety and diverse nature of this waste.[3,4] The only statement found concerning the leachability of existing TRU waste is that conservative estimates indicate leach rates less than or equal to the dissolution rate of rock salt in water and in

some cases possibly equivalent to that of HLW glass for an estimated leach rate range of 10^{-7} to 1.0 g/cm^2-d. This range seems realistic for some of the actinides since they occur in forms of extremely low solubility. At this time, then, no credit can be given to as-generated TRU waste as a major barrier in the controlled release of actinides. Based on this assumed leachability for existing TRU waste, the consequence analysis predicts that none of the credible liquid breach scenarios investigated would result in a significant release of radionuclides to the biosphere.[4] Any future analyses are expected to replace the leachability assumption if experimental data show that phenomena such as leaching, waste matrix degradation, and the valence states of the radioactive species significantly affect the release rates. It is also planned to investigate experimentally the leachability of both combustible and noncombustible wastes.[2] Questions have been raised[2,5] regarding such issues as verification of radionuclide transport codes with field data, and these may still have to be resolved.

2.3 Conventional TRU Waste Forms

This Section deals with the waste forms presently in use for immobilizing ash waste from the incineration of combustible TRU waste and some wet TRU waste for which information has been collected and reviewed. These waste forms include bitumen, cement/concrete, and urea-formaldehyde resins. Bitumen solidification systems are not used in the U.S. but find widespread application in foreign nuclear facilities. Some of the waste types that are treated by these immobilization technologies are listed in Table 2.1. Incinerator ash

Table 2.1

Fuel Reprocessing Plant Particulate and Wet Wastes
(This is Table 4.7.1 of Reference 6)

Source	Description
Fuel receiving and storage facility	Mostly non-TRU, intermediate-level solutions and slurries of ion exchange resins, filter aids, and concentrated solutions
Separations facility	Primarily intermediate-level TRU concentrated solutions and slurries
PuO_2 conversion facility	Low-level TRU solutions and slurries (volumes would be combined with separations facility wastes)
UF_6 conversion facility	Low-level; little or no TRU content; low water content; composed of oxides, hydroxides, and fluorides
Waste treatment facilities	Secondary wastes arising from waste treatment operations, including incinerator ashes, off-gas scrub solutions, and decontamination solutions

compositions are given in Table 2.2 for ash generated at the Rocky Flats Plant (RFP) from the fluidized bed incinerator (FBI) system and the conventional incinerator. No TRU contaminated waste has been incinerated in the fluidized bed incinerator.[7]

2.3.1 Bitumen (Asphalt)

2.3.1.1 Physical and Chemical Properties

Bitumen is a mixture of high molecular weight hydrocarbons commonly obtained as a residue in petroleum and coal-tar refining. The elementary composition of asphalts free of minerals, water, and gases is as follows: carbon (80-86%), hydrogen (9-11%), oxygen (1-17%), sulfur (1-9%), nitrogen (1%), and ash (0.1-1%). These elements occur in four major components: saturated hydrocarbons, resins, cyclic hydrocarbons, and asphaltenes in various proportions.

Table 2.2

Composition of Incinerator Ash
(This is Table 1 of Reference 7)

Component	Quantity in Ash[a] Fluidized Bed (wt%)	Conventional (wt%)
Pu	b	4.6
Am	b	5.4×10^{-3}
SiO_2	9	48
C	26	17
Fe_2O_3	0.5	5.7
MgO	1.0	4.0
CaO	1.0	4.0
Al_2O_3	4.9	c
Na salts	23	d
Other	35	16

[a] Single determination.
[b] Low level; total count $<10^3$ dpm/g ash.
[c] Negligible; large amounts in FBI ash from catalyst in afterburner.
[d] Negligible; large amounts in FBI ash from Na_2CO_3 (fluidized medium).

At ordinary temperatures, bitumen appears to be a lyophilic colloid made up of asphaltenes, resins, and hydrocarbons. As the temperature of asphalt is increased (25° to about 500°C), colloidal structure is changed and the fluidity of the substance increases. When cooled to 25°, the product is normally more prone to be brittle than it was originally. This is important if this waste form is subjected to changes in ambient temperature under repository or possible interim storage conditions. The density of bitumen ranges from 1.1 to 1.5 g/cm^3. The waste form, loaded with 40 to 60% solids, has high mechanical strength and no residual free water. Little detailed information has been accumulated on the leach resistance of bitumen. However, since its constituents are highly insoluble in water, low rates are expected. The ranges that have been published for rare earths and actinides are 10^{-7} to 10^{-3} g/cm^2-day,[8] and 10^{-7} to 10^{-8} g/cm^2-day.[6] Parameters such as percent loading, temperature, type of leach test, etc., were not available. Release rates for bitumen can be estimated if one assumes a geometry for the monolith. A typical waste container might be a 55-gallon drum (24 in. x 35 in.) that is filled to 90% of its volume. For a bitumen/waste matrix of density 1.3 g/cm^3 and a leach rate of 10^{-7} g/cm^2-day, an initial annual fractional release rate of 2.5×10^{-6} is estimated.

2.3.1.2 Stability

The thermal stability of bitumen products is good at ambient to moderate temperatures, fair at moderate temperatures, and poor (ignition results) at high temperatures. Certain salts were found to have adverse effects on the thermal stability of bitumen. Nitrates and nitrites, which are known oxidants, have been investigated because of their use in fuel reprocessing. It was found that the bitumen containing 40 to 75% (w/w) sodium nitrate/nitrite salts had lower ignition temperatures. The bitumen, although demonstrated not to be explosive,[9] burned more vigorously when significant amounts of oxidants that decompose at the combustion temperature were present.[8] Ignition temperatures for various grades of bitumen range from 260° to over 400°C.[9] Tests were conducted to determine if combustion of bitumen was possible by ignition of hydrogen-air mixtures resulting from the radiolysis of the bitumen. Initial small-scale experiments with H_2 contents between 4 and 11% (v/v) did not result in inflammation of the bitumen sample. The working temperature range for waste bitumenization processes is 150° to 230°C. This operating range is a disadvantage because of the generation of volatile organic compounds (potential fire hazard)[9] and because the resultant condensate is an additional waste stream that requires disposal treatment.[6] The concern for the secondary waste stream depends on its TRU contaminant level.

Insufficient data exist for assessment of the long term chemical stability of bitumenized radioactive wastes under geologic repository conditions (potential leaching scenarios, waste/container and waste/rock interactions, etc.).

Various bitumen types and bitumen/salt mixtures (about 40% by wt. salt) were subjected to gamma radiation.[9] A marked increase in the softening point was observed for blown bitumen and its corresponding product when

irradiated to 5 x 10^8 rad. All pure bitumen and bitumen/salt samples showed significant swelling under these same exposure conditions. The increase was as high as 70% (v/v), presumably caused by radiolytic gas generation. As will be discussed in Section 4, hydrogen and methane are generated by alpha radiolysis of bitumen and carbon dioxide by microbial degradation. Preliminary results indicated that significant quantities of methane could potentially be generated by microbial degradation of this waste form under appropriate conditions. ZoBell and Molecke[10] have addressed several areas that concern the possibility of radionuclide migration due to microbial metabolic processes involving bitumen.

At this time, much information on the performance of bitumen as a suitable waste form for TRU immobilization is incomplete and/or inconclusive. The high volumetric efficiency (waste loading), waste types applicable, and leach resistance of bitumen argue in favor of its use. However, based on its stability to thermal, radiolytic, and microbial attack, it does not appear that bitumen is capable of meeting NRC repository criteria. We also feel that further research on this waste form should be discontinued because its chemical and physical properties and flammability preclude the successful development of techniques that might make it an acceptable form.

2.3.2 Urea-Formaldehyde Resins

The immobilization of radioactive wastes in urea-formaldehyde (U-F) is a well developed technology that is widely applied in U.S. nuclear facilities. The resin is used to incorporate aqueous waste solutions, filter sludge, and ion exchange resins. Recently, work at Brookhaven National Laboratory (BNL) has been reported on leaching of U-F waste forms incorporating actual TRU incinerator ash.[11]

2.3.2.1 Physical and Chemical Properties

U-F is a condensation product of urea and formaldehyde which react under neutral or alkaline conditions to yield monomethylol or dimethylol urea. As a solidification agent, the cross linked U-F polymer entraps the waste (about 50% loading) within its structure. Because the hardening reaction is acid catalyzed, the trapped water is acidic (pH 1 or 2) and, hence, corrosive. The U-F emulsion is completely miscible with water but immiscible with non-polar solvents.

The density of U-F is 1.3 g/cm^3 (25°C) and the density range for the immobilized U-F waste product is 1.0 to 1.3 g/cm^3. U-F is slightly basic (pH of 7.4 to 7.8) and has a low free formaldehyde content. Significant amounts of free water (that are not bound by the solid waste form) have been observed for some U-F formulations under certain conditions. As much as 26% (w/w) free water was found for decontamination waste (waste/U-F ratio = 0.5).[12] Free standing water can potentially lead to nuclide migration and container corrosion, not to mention radiolytic gas generation. The mechanical strength (i.e., compression and impact strength) of U-F, compared to cement, is rated as fair.[8,13]

The BNL leaching studies were carried out on samples prepared using a small amount of actual "hot" incinerator ash from the dual chamber burner incinerator at RFP, mixed with nonradioactive ash from RFP's rotary kiln incinerator. The composition of the "cold" ash is given in Table 2.3, and this was very close to the final composition of ash used in the samples, since the weight ratio of hot to cold ash was <1:20.

Table 2.3

RFP Rotary Kiln Incinerator Ash Composition
(This is Table 2 of Reference 11)

Element	Weight %
Al	18
C	13.1
Si	>10
Ca	5
Ti	4.8
Zn	2.6
Mg	1
Na	0.5
Fe	0.3
K	0.1
Ni	0.1

The hot ash contained 9 wt % plutonium, mostly as Pu-239. The U-F waste form samples contained 63.5 wt % U-F emulsion, 18.6 wt % incinerator ash, 16.7 wt % water and 1.2 wt % $NaHSO_4$. The density of the resulting solidified waste forms averaged 1.5 g/cm^3.

Two types of leach tests were performed--modified IAEA and static, both at 25°C. Several different leachants were used, including demineralized water, simulated WIPP brine "B", and a simplified bicarbonate dominated groundwater, but only demineralized water was used in the static tests. Results of the modified IAEA tests showed leach rates decreased from approximately 10^{-4} to 10^{-7} g/cm^2-day after 100 days for groundwater leachants and after a week for brine and demineralized water, and then remained steady. These rates vary from only slightly higher to 2 orders of magnitude higher than the comparable rates for Portland I cement. The leach rates in the static test, however, were approximately 3 orders of magnitude higher than those of Portland I cement.

2.3.2.2 Stability

Several samples of various water/U-F emulsion ratios underwent rapid and complete dewatering within five days on exposure to ambient air (20°C) and 50% relative humidity. The effect of water loss on mechanical properties and leachability has been discussed elsewhere.[12] Potential concerns over the release of water in a geologic repository are addressed in Section 4.4.3. Various U-F formulations were subjected to a standard flammability test and found to undergo minor surface charring; no sustained burning for any length of time was observed.[12] This is partially due to the water content of the resin.

Hydrogen gas was generated due to gamma radiolysis of the water contained in U-F. Hydrogen yield decreased with increasing total dose, probably due to attainment of steady-state conditions. This phenomenon is observed in the gamma radiolysis of water. Although no information is available on the alpha radiolysis of U-F, hydrogen is expected from the radiolysis of water. However, due to mechanistic differences, the hydrogen pressure will most likely continue to increase with increasing total dose. The accumulation of explosive atmospheres within waste containers due to hydrogen formation is an area of concern that is discussed in Section 4.4.2.4.

It has not been determined if U-F products undergo bacterial degradation and concomitant gas production. Bacterial growth can be supported by nutrients that are leached from the waste matrix by groundwater. The analysis of leachant from a U-F sample showed that a significant amount of organic carbon is leached from this waste material (about 4% of the total carbon content after only ten days of static leaching).[12] The form of the organic carbon and whether it was capable of supporting microbial growth were not determined. The microbial degradation of waste matrices can result in generation of explosive gas mixtures with dispersion of radionuclides, increased leachability, and loss of waste package integrity.

Urea-formaldehyde resin is deemed an unacceptable waste form for immobilization of TRU wastes. Because of its water content (which is corrosive), instability toward radiolytic degradation with consequent gas production, potential for microbial degradation, mechanical strength and relatively low leach resistance, this waste form cannot (and probably would not with additional R&D) meet NRC repository acceptance criteria.

2.3.3 Hydraulic Cement/Concrete

The use of concrete for immobilization of low level and intermediate level radioactive wastes (LLW and ILW) has found wide application in the U.S. for many years. It is also used at several DOE sites for immobilization of certain defense TRU wastes. This waste form is considered attractive because the raw materials are inexpensive, ambient temperatures are used for processing, and processing operations are fairly simple. The literature reviewed to date deals with fixation of liquid concentrates and solid waste

(generated as by-products of the liquid radwaste treatment in LWR's), and immobilization of actual TRU incinerator ash.

2.3.3.1 Physical and Chemical Properties

A mixture of hydraulic cement, water, and aggregate is known as concrete. Three commonly used types of cement are portland cement, portland-pozzolanic cement, and high alumina cement. The major constituents are various calcium silicates and aluminates. Five types of portland cement have been defined and consist mainly of tricalcium silicate ($3CaO \cdot SiO_2$), dicalcium silicate ($2CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$), and tetracalcium aluminoferrite ($4Ca \cdot Al_2O_3 \cdot Fe_2O_3$). Relative compositions of types I-V portland cement are given in Table 2.4. Type I-P cement is a standard portland-pozzolanic cement with 80% type-I plus 20% fly ash (SiO_2). Fly ash enhances the cementitious properties of portland cements by reacting with the calcium hydroxide formed during the hydration of cement. High alumina cement (HAC) is composed primarily of monocalcium aluminate ($CaO \cdot Al_2O_3$).[14] Hydration reactions are responsible for the setting and hardening of cement paste into concrete. For portland type cements, cementitious hydrates and calcium hydroxide are the reactants. In portland-pozzolanic cements, the pozzolan (fly ash) reacts with $Ca(OH)_2$ to form compounds that possess cementitious properties. High alumina cement reacts with water to form cementitious, hydrated calcium aluminate and aluminum hydroxide.[14]

Table 2.4

Relative Composition of Portland Cements
(This is Table 1 of Reference 14)

	Composition, wt %			
Cement Type	C_3S[a]	C_2S[b]	C_3A[c]	C_4AF[d]
I	45	27	11	8
II	44	31	7	13
III	53	19	10	7
IV	20	53	6	14
V	38	43	4	8

[a] Tricalcium silicate - $3CaO \cdot SiO_2$.
[b] Dicalcium silicate - $2CaO \cdot SiO_2$.
[c] Tricalcium aluminate - $3CaO \cdot Al_2O_3$.
[d] Tetracalcium aluminoferrite - $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

Before additional properties are discussed, some mention of the types of wastes that are being incorporated into concrete will be made. As was indicated above, LWR liquid concentrates and wet solids from radwaste

treatment consitute the LLW and ILW requiring disposal. The wet solid waste is comprised of spent resins, filter sludges, evaporator concentrates and miscellaneous liquids. Hanford Engineering Development Laboratory has conducted studies on the immobilization of TRU contaminated dehydrated residue (from acid digestion processing), filter residue, and ion exchange resin. Savannah River Laboratory (SRL) has studied the incorporation of HLW simulated sludges and actual HLW radioactive sludge into concrete. Sludge compositions are given in Table 2.5.[15] The gross alpha activity ranged from 0.1 to 0.3 mCi/g. Incorporation of simulated Hanford HLW in concrete has also been studied. The compositions of these simulated sludges are given in Table 2.6.[14] The work being conducted at SRL and Hanford is directed at the disposal of defense high level waste. BNL has investigated the leaching of plutonium from Portland I concrete containing 30 wt % RFP rotary kiln incinerator ash which included a small amount of actual TRU incinerator ash from the RFP dual chamber burner incinerator. The composition of the rotary kiln ash is given in Table 2.3.

2.3.3.2 Stability

Cement/waste composites must exhibit sufficient strength to withstand handling, transportation, and accident situations with only marginal resultant damage. Neat cement pastes exhibit compressive strengths of approximately 69 MPa with portland cements developing about 90% ultimate strength after 30 days and high alumina cements developing about 75% after only 3 days. Compressive strengths of cement-sludge samples progressively decrease with increasing sludge content; the decreases are primarily due to the lack of strength of the sludge particles. Compressive strengths for simulated sludges are listed in Table 2.7.[15] Neat cement pastes receiving gamma radiation exposures during curing

Table 2.5

Composition of Washed, Dried SRP Waste Sludges
(This is Table 4 of Reference 14)

	Wt % Element in Sludges from SRP Tanks		
	Tank 5	Tank 13	Tank 15
Fe	27.5	27.9	3.1
Mn	10.8	8.8	2.3
Al	1.5	7.1	33.5
U	15.4	4.0	0.9
Na	6.1	3.1	1.2
Ca	0.6	2.3	0.2
Hg	0.1	2.1	0.9
Ni	5.1	0.5	0.5

Table 2.6

Composition of Simulated Sludges, Wt %
(This is Table 3 of Reference 14)

	Hanford Redox Sludge	Hanford Purex Sludge
Fe	2.7	22.4
Al	22.6	8.3
Mn	0.09	2.5
Sr	1.8	1.0
Na	3.9	4.8
Cr	1.9	--
Si	5.2	6.4
Ca	--	0.5
PO_4^{3-}	--	2.2
H_2O	30.0	26.0
O_2[a]	31.0	26.0

[a] Calculated.

Table 2.7

Compressive Strength of Concrete Waste Forms
(This is Table 6 of Reference 15)

SRP Simulated Sludge		Compressive Strength (psi) Cement Types					
Type	Wt %	I	II	III	V	I-P	HAC
	0	10 824	11 284	13 478	11 898	11 916	9 311
I	10	8 402	8 243	8 694	8 829	8 296	9 574
	25	4 588	4 630	6 180	5 620	4 472	5 792
	40	464	1 259	1 546	3 054	2 380	4 364
II	10	8 973	9 045	9 321	11 159	7 692	9 624
	25	5 779	6 412	7 230	7 158	5 855	7 158
	40	3 932	3 352	4 736	4 234	3 311	5 884
III	10	9 313	7 557	7 603	8 490	7 761	8 465
	25	5 171	4 627	5 817	4 732	4 930	6 658
	40	2 388	2 884	3 317	2 700	3 088	3 371

exhibit lower compressive strengths than normally cured samples. The strength of high alumina cement containing simulated sludges is not affected by heat or radiation during curing. The same effect of waste additions is seen for steam cured samples, i.e., strength is decreased in neat pastes but unaffected by sludge additions. Specimens heated at 100°C for 3 months exhibit about 25% lower strengths than unheated samples of identical formulation. Gamma irradiation effects on the strength of cured samples are minimal. Sorbents alone tend to decrease strength; however, formulations with sludge plus sorbent exhibit strengths that are higher than those of formulations with sludge or sorbent alone.[14] Compressive strength is a measure of the stress required to fracture or plastically deform a material. Since no correlation of strength and safety has been developed, workers at SRL have also conducted impact tests on solid waste forms. In the tests, samples are broken by impact of known energy and the particle size distribution of the sample is determined after impact. The results of this type of test are considered important because the creation of a large number of small particles increases surface area and the potential for leaching. The surface area, A, created by impact with energy input, E, may be a useful parameter in defining the safety of solid waste forms. Typical values of A/E for various waste forms are given in Table 2.8.[16] The particle size distribution resulting from impact is also an important consideration because the production of excessively small particles increases the potential for creating an airborne hazard.

Table 2.8

Relative Impact Resistance of Various Waste Forms
(This is Table 9 of Reference 14)

Waste Form	Surface Area Increase Per Joule Input[a] A/E, cm^2/J
Glass with 45% Sludge	9.5
Neat HAC	7.3
Neat I-P	10.3
HAC + 40% Sludge	28.9
I-P + 40% Sludge	19.4
Portlant III + 40% Sludge	25.3

[a] 8 kg-m input for glass; 9.6 kg-m input for concrete forms.

Leachability of alpha radioactivity from concrete waste forms containing actual SRP sludges was very small and near the limit of detection. Actual values ranged from about 10^{-5} g/cm^2-d initially to about 10^{-8} g/cm^2-d after six weeks with less than 10^{-3}% Pu leached after six weeks. Consistent with cesium and strontium leachability, alpha emitter leachability was a strong

function of time; however, the data more closely followed at t^{-1} relationship (rather than $t^{-1/2}$), indicating that leachability was controlled by factors other than simply diffusion within the matrix. These results are similar to those obtained from concrete waste forms containing simulated SRP sludges. Plutonium leachabilities from samples containing 5×10^7 dis/min of Pu-239, which ranged from 10^{-5} g/cm^2-d initially to 10^{-8} g/cm^2-d after 12 weeks, were strong functions of time, and were relatively unaffected by cement type, sludge type, and sludge content.[15]

Leach rates for plutonium from simulated ILW cement products have been determined in four different leaching media.[17] Plutonium leachabilities in deionized water, 0.01 M NaCl solution, and 1 M NaCl solution were comparable and ranged from $2\text{-}11 \times 10^{-7}$ g/cm^2-d. In saturated carnallite solution, the plutonium leach rate after 35 days was about 5×10^{-5} g/cm^2-d. Carnallite solution corresponds to an equilibrium solution from water leached natural salt deposits; its composition includes 62.83 wt.% H_2O, 2.04%, $MgSO_4$, 34.3% $MgCl_2$, 0.62% KCl, and 0.21% NaCl.

The BNL leach study[11] was carried out on portland cement waste forms containing 0.3 wt % plutonium, mostly Pu-239. A modified IAEA test and a static test were used, both at 25°C, with a number of leachants, including demineralized water, simulated WIPP brine "B", and a simplified bicarbonate dominated groundwater. Results of the modified IAEA tests showed that, after the first week, leach rates were between 10^{-7} and 10^{-8} g/cm^2-d with demineralized water and bicarbonate dominanted groundwater, and approximately 10^{-9} g/cm^2-d with simulated WIPP brine "B". The static tests gave comparable results, except that the bicarbonate dominated groundwater gave lower leach rates than in the modified IAEA tests. These results indicate very good Pu leach resistance for this particular waste concrete formulation.

Gas generation problems associated with, and the consequences of, alpha radiolysis of concrete containing simulated process sludge or TRU incinerator ash will be discussed in Section 4.4.2.3 of this report. Also discussed are techniques and additives that help minimize the importance of gas generation for long term disposal of TRU waste in concrete. Suitability of hydraulic cement (cast concrete) as a waste form, based both on its potential for gas generation and its leach resistance, is considered in the conclusions of the waste form section (Section 2.11), where its qualifications are compared to those of specially prepared concretes.

2.4 Iron-Enriched Synthetic Basalt

The leading contender for immobilization of the transuranic waste stored and buried at INEL is a waste form that is similar in composition to natural basalt but has a somewhat higher iron content. Thus, it has been dubbed "Iron-Enriched Synthetic Basalt (IESB)." It had been intended that this product would be the end result of a process known as Slagging Pyrolysis Incineration (SPI). The basic process, known as the "Andco-Torrax Process," was developed for treatment of municipal refuse but has yet to be proven in radioactive service. The SPI process was chosen as the reference process for the Trans-

uranic Waste Treatment Facility proposed to reduce the TRU waste inventory at INEL to a solid waste form.[18] A slightly different slagging incineration design has been in use at the S.C.K./C.E.N. Nuclear Energy Research Center in Mol, Belgium for the processing of TRU contaminated waste. The resultant amorphous waste product has been described as having a basalt-like appearance. Pertinent information from the Belgian waste form characterization effort will be included in the discussion of the IESB product.

2.4.1 INEL TRU Waste Processing

We will only briefly describe the SPI process here for two reasons: (1) The method has been adequately described elsewhere,[18-20] and (2) according to recent information,* the use of the SPI process for conversion of the INEL waste inventory is undergoing careful scrutiny for reasons to be discussed later.

It is projected that some 4×10^5 m^3 of buried and stored TRU waste will have accumulated at INEL by the year 2000. Most of this waste is in the form of sludge. The SPI process is designed to handle combustible and non-combustible materials, with minimal pre-sorting, and also contaminated soil (estimated to be between one and two tons). A mixture of TRU waste and soil is fed into the incinerator along with supplemental fuel (coal and bark) to produce slag. The temperature in the "hearth" is reported to be 1650°C.[20] The slag can then be tapped from the bottom of the SPI into a water tank. The resultant frit must be remelted in order to achieve complete oxidation of metals and carbon, and also to achieve product homogeneity.

A second method for producing the basalt-like product involves electrical heating via an Electric Melting Furnace (EMF). Our understanding of this process is that energy is supplied by passing an electric current through the conductive molten slag, while combustibles are burned on the surface. Typical temperatures in the melting zone are approximately 1400°C. To date, most of the characterization assessments of synthetic slag wastes have been performed on lab scale melts (approximately 50 to 200 g) prepared in conventional high temperature furnaces. Apparently, these melts are highly vitreous[21] and it was felt that they were not representative of large scale melts and castings that would occur from a combined SPI-electromelt process. Thus, INEL had Penberthy Electromelt (Seattle, WA) prepare several large scale (38-cm diameter x 43-cm high, approximately 90 kg) castings of IESB for product characterization and assessment. This assessment included evaluations of solidification patterns, devitrification (plus phase and structure analysis), porosity and cracking, composition homogeneity, slag/canister interaction, chemical durability and mechanical properties. Our evaluation of IESB** will mainly address the results of these studies on the large scale electromelt slag castings. While we are aware of additional work being performed at INEL on lab scale melts of IESB, published data were not available for our review at the time of this writing.

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*D. Owen, EG&G Idaho, Inc., private communication to G. Bida, BNL, May 11, 1981.
**It is our understanding that IESB refers to the final product from the electromelt process and not to the glass frit that results from water quenching of SPI slag.

2.4.2 Properties and Characterization

2.4.2.1 Preparation and General Structural Characteristics of Slag Castings

Basalt is an igneous rock composed mainly of silicates of magnesium, aluminum, calcium, and iron. They are generally subdivided according to chemical composition and mineralogy into three groups: tholeiites, olivine basalts, and basanites. Specific basalt compositions can be found in the literature;[22] however, for the sake of comparison with the reported INEL slags (see below), we have listed an average chemical composition in Table 2.9

Table 2.9

Average Chemical Composition of Basalt
(From Table 7.2.1 of Reference 22)

Compound	Wt %
SiO_2	49.1
Al_2O_3	15.7
Fe_2O_3	5.4
FeO	6.4
CaO	9.0
Na_2O	3.1
K_2O	1.5
MgO	6.2
H_2O	1.6
Other (e.g., MnO, TiO_2)	2.0

The four castings prepared by Penberthy Electromelt that underwent detailed examination at INEL were produced from compositions that represent the major oxide components of an average INEL low level TRU waste mixed with soil (see Table 2.10). The slag waste compositions were designated "A" series slags, i.e., A-0, A-20, etc., to indicate average waste composition while the numbers indicate the weight percent of soil added to the average waste composition. The compositions prepared for INEL analysis had a soil content that was varied from zero to 40% (w/w): A-0, A-20, A-30, and A-40. For slags A-20 and A-30, actual INEL soil was used along with commercial raw materials in powder form. The soil and powders were premixed and charged into the melter, a process that normally took one day to complete. The melter was held at 1300° to 1480°C overnight with pouring accomplished the following day. The canisters used to contain the molten slag were galvanized steel and/or mild steel. Cooling curves were obtained for most of the castings by placing thermocouples on the outside wall of the canister and inside the container via a closed end steel well.[23] Observations and conclusions regarding the production of large scale IESB monoliths are summarized below:

Table 2.10

Estimated Composition of Average Waste
(This is Slide No. 6 From Reference 24)

Constituent	Wt %
SiO_2	38.0
Al_2O_3	7.4
Fe_3O_4	34.5
CaO	8.3
MgO	4.6
Na_2O	4.8
K_2O	2.4

(1) The castings were sectioned in half for characterization purposes. Large cavities, comprising roughly 10% of the total volume of the casting, were observed for all four compositions. It has been speculated that this may be due to air entrapment during pouring of the molten slag.[24]

(2) A friable crust layer (approximately 0.5-cm thick) was observed in all cases, probably due to a faster cooling rate on the surface than in the interior since it was directly exposed to air.[23] Also, a high iron content apparently promotes crust formation.[23] The nature and consequence of this layer were not detailed; however, it is felt that the crust layer problem can be minimized via a hot zone above the melt.

(3) Iron appeared to aid the electromelt process by increasing the electrical conductivity, thereby eliminating the need for alkali addition. As will be discussed below, this is an important consideration in regard to the waste form's chemical durability.

(4) The thermal conductivity of the slags was found to be very low.[23] This property, attributed to the presence of FeO, was considered a disadvantage in processing Hanford salt cake into a basalt glass product[25] because of resultant undesirable thermal gradients. Related to the thermal conductivity of the slags, the cooling curves for the A-0 and A-20 slag compositions displayed a "thermal arrest" between 1150° and 1200°C.[23] This is possibly due to crystal growth of the diopside solid solution or spinel phases (see Section 2.4.2.2). It has been found that the amount of iron oxide that can be incorporated into a glassy silica matrix is a function of the cooling rate.[26] The iron content, in turn, will affect the chemical durability of the glass phase.

(5) The degree of porosity of the slags was measured and ranged from 8-12%.[23]

(6) All castings displayed both large cracks and an extensive network of microcracks[24] that increased with increasing iron content.[23] The effect of this feature on leachability and mechanical properties will be discussed below.

(7) The overall grain size of the products near the canister walls was finer than that at the center of the castings and also finer than for basalt found near the INEL site.[23,24] The fine grain size is due to the relatively rapid cooling (approximately 24 hours) of the slag as compared to natural basalt. It is anticipated that slower cooling will decrease the extent of interior cracking and will yield a coarser grained, more devitrified product.[23] Both features should give a more chemically durable waste form.

(8) The thin walled mild or galvanized steel containers were determined to be quite adequate for molten/solidified slag containment. No significant slag/canister interaction was observed.[23]

(9) Soil additions presented no difficulties to the electromelt process.

Plug-type specimens were removed from the castings and subjected to tensile and fracture toughness analyses, SEM, EDS, and XRD analyses, metallography, chemical analysis, and leach testing. The results of these examinations are discussed in the sections that follow.

2.4.2.2 Physical, Chemical, and Microstructural Characterization and Mechanical Properties

Casting homogeneity was determined by density measurements and chemical analyses. The mean density for measurements made on three specimens taken from each of the four castings is 3.08 ± 0.10 (one std. dev.)g/cm^3.[23]

Compositional analyses to determine homogeneity included silica, alumina, total iron, Ca, Mg, K, and Na. Based on the average composition of INEL waste and the composition of soil from INEL, the addition of soil is seen to decrease the iron content and to increase the silica content of the waste slags. The compositional variation of the A-series slags due to soil addition is shown in Figure 2.1. The experimentally measured average compositions of the A-series slags are given in Table 2.11. As can be seen by comparison with Table 2.9, the A-40 composition most closely resembles basalt since it has a silica content of about 50 wt %. The slag casting designated A-30 was originally formulated by adding 60 wt % soil to the average waste. However, the average composition of the A-60 casting was found to be markedly different from the calculated values based on the major oxide constituents. In fact, the average composition of the A-60 casting is more representative of that calculated for an A-30 slag.[23] For this reason, this particular composition is referred to as A-30 in this report. In general, each casting was found to be compositionally homogeneous.

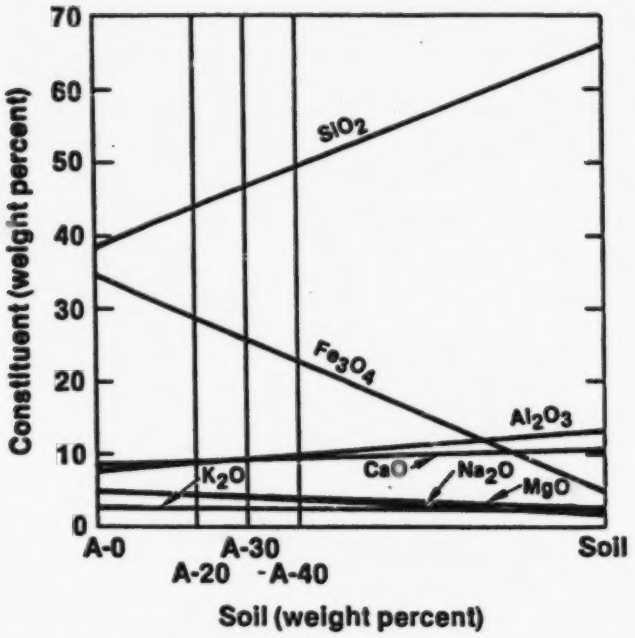

Figure 2.1 Effect of Adding Soil to Average Waste (This is Slide No. 7 From Reference 24).

Table 2.11

Nominal Chemical Composition of A-Series Electromelt Slags (This is Table 1 of Reference 21)

Slag	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	K_2O	Na_2O
A-0	40.4	10.2	15.6	14.8	0.07	8.6	3.4	1.8	5.0
A-20	42.9	10.6	9.8	15.8	0.30	10.8	3.3	1.9	4.4
A-30	47.8	11.0	2.5	19.6	0.24	9.6	2.9	2.1	4.2
A-40	51.3	11.0	6.1	11.7	0.05	9.8	2.4	1.7	6.0

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The only anomalous results were for the A-30 casting. Both the iron content and the Fe^{2+}/Fe^{3+} ratio were higher than anticipated. It is speculated[23] that the high FeO content may be due to the use of iron electrodes in the electromelt process and/or the fact that the A-30 melt involved the highest processing temperature.

Crystalline phases were determined by X-ray diffraction, while microstructure and elemental analyses were accomplished by optical microscopy, SEM, and EDS. The A-series slags were found to consist of three phases: pyroxene, spinel, and an amorphous glass matrix. The pyroxene phase has been identified as diopside, a chain silicate ($CaMgSi_2O_6$), in solid solution with other closely related minerals.[23] A later report[24] described the pyroxene phase as augite, of which diopside is an example. Augite has the general structural formula $(Ca,Mg,Fe,Al)_2(Si,Al)_2O_6$ and is essentially diopside with components such as $MgSiO_3$, $CaFeSi_2O_6$, $CaAl_2SiO_6$ and $NaFeSi_2O_6$ likely to be present in solid solution.[27] The pyroxenes do not incorporate much alkali in solid solution, thus leaving the residual glass phase alkali-rich and susceptible to relatively high leachability.

The spinel phase is iron-rich magnetite (Fe_3O_4) with minor amounts of Mg, Al, Cr, Mn, and Ti in solid solution.[23,24] The residual glass phase is an aluminosilicate enriched in alkali (Na^+ and K^+). Relative amounts of crystalline and glass phases in the slag castings were determined by micrographic image analysis. Although all four castings contained some residual glass, they were found to be 75 to 90% devitried.[23] This is an interesting observation since the granular FLK slag, similar in composition to IESB, has been qualitatively described as mainly amorphous.[28] Also, basalt glass ceramics that were prepared via controlled crystallization were only 50 to 60% crystalline.[27] Additional observations were: (1) The number and size of the spinel grains decreased with decreasing total iron and/or Fe_2O_3 contents, i.e., trivalent iron is necessary for spinel phase formation. The effect of iron oxidation state on nucleation and crystal size in basalt glass ceramics has been observed elsewhere.[27] (2) The degree of devitrification increased and grain size decreased (indicating pyroxene phase formation) as the iron content decreased.

A third crystalline phase has been reported[24] for lab-scale melts that underwent controlled cooling to promote devitrification. The sample was found to contain anorthite-rich plagioclase feldspar ($CaAl_2Si_2O_8$) in addition to augite and spinel phases. This phase is known to incorporate Na, K, and Fe into its structure. It is possible, then, that controlled cooling of slag melts under the appropriate conditions could yield a product that is low in alkali-rich glass phase if the alkali content can stabilize an alkali bearing phase such as feldspar. With a lowered residual glass phase content, IESB should have a greater leach resistance. Work in this area is under way at INEL.

The same three crystalline phases, i.e., augite, spinel, and feldspar, that were observed in the INEL slag castings have also been found in other studies involving basalt glass ceramics.[27,29] The latter work has shown successful production of basalt glass ceramics using Hanford basalt and 20 wt % PW-9 simu-

lated waste calcine. In all the literature we have reviewed to date, one obvious question remains unanswered. Since IESB is meant to immobilize INEL TRU waste, into what phase(s) are the transuranic ions incorporated? It has been stated that neither augite nor spinel contain crystallographic sites large enough to accommodate transuranic ions.[24] Furthermore, few chemical substitutions are allowed in feldspar minerals.[30] Brief reference has been made to experiments conducted at INEL in which a lab-scale glass melt containing approximately 2 wt % U_3O_8 was prepared to determine its leaching behavior.[24] Other work from INEL on the preparation of U-doped slag castings has shown that the melts are essentially vitreous and the uranium remained in the silica-rich (glass) regions.[31] Since that time, we have received additional information concerning the location and partitioning of actinides in IESB*. Apparently, the TRU waste at INEL can be conveniently divided into two types: low level, in which the TRU nuclides are present in concentrations of parts per million or less, and higher levels, in which the TRU elements are present in quantities greater than 1%. For IESB that contains the latter amount of TRU, sufficient concentrations of TRU element oxides exist to stabilize a UO_2-type phase (uraninite) for a nearly completely devitrified product. At lower TRU concentrations, sufficient quantities of TRU are not present to stabilize a crystalline phase. Transuranics are then expected to partition into the residual glass phase. Based on the behavior of trace elements in natural rock systems, it is expected that the crystalline phases of IESB will not be devoid of TRU but the concentration of TRU in the glass phase will be greater than TRU elements in crystalline phases. Certainly, the formation of actinide-bearing phases and actinide partitioning in IESB are areas that require more detailed work. Experiments along these lines are in progress at INEL.

Mechanical properties testing of A-series slag casting specimens included splitting tensile strength (commonly used to evaluate the ability of concrete to withstand tensile stress), fracture toughness (measure of a material's resistance to fracture), microhardness, and crack propagation due to intentional indentation of the specimens. A qualitative description of the results of these tests is given below.

(1) Splitting tensile strengths were reported for A-0, A-20 and A-30 samples.[23] The strengths of A-0 and A-30 were found to be lower than for A-20. This behavior has been attributed to the possibility that the A-20 sample had a higher density of microcracks than the other two compositions and thus required more energy to propagate the microcracks. The microhardness of borosilicate glass was roughly a factor of three greater than for the IESB samples.

(2) Fracture toughness values for the slags were lower than for borosilicate glass.[23] Again, this has been attributed to the extensive microcracking observed in the slag melts. However, the toughness values did not correlate with the amount of microcracking.

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*Letter from J. M. Welch, Idaho National Engineering Laboratory, to G. Bida, BNL, Subject: Information on Iron-Enriched Synthetic Basalt (IESB), dated January 29, 1981.

(3) Microhardness measurements for the slag castings did not correlate with composition. Also, differences in microhardness and measured microcrack lengths produced by indentations showed no apparent correlation with the phases present.[23]

2.4.2.3 Chemical Durability

The leaching behavior of the IESB product was determined in accelerated static leach tests performed on samples from each of the four castings.[21,24] (Another reference has described the tests as semistatic, but the frequency of leachant change was not mentioned.[23]) Rectangularly shaped monoliths (2.3-2.9 g) having a geometrical surface area of 5.5 cm^2 were suspended in 70°C deionized water for 14 days. Elemental leach rates were determined by emission spectroscopy and their sum (as oxides) was compared to the bulk dissolution rate determined from weight loss measurements. The results from the two types of measurement are listed in Table 2.12. The leach rates from the elemental analyses and weight loss measurements are comparable.

Table 2.12

Leaching Results for Electromelt Slag Specimens
(Data Taken From Table 2 of Reference 21)

Slag Type	Bulk Dissolution Rate ($\mu g/cm^2$-d)	Total Oxide Leach Rate[a] ($\mu g/cm^2$-d)
A-0[b]	27.2	31.0
A-20[b]	20.9	22.7
A-30[c]	14.8	18.2
A-40[b]	8.9	11.7

[a]From leachant analyses, converted to oxides.
[b]Average of three determinations.
[c]Average of four determinations.

The dissolution rates given in Table 2.12 are about a factor of ten higher than those reported for vitreous lab scale melts leached under similar conditions.[31] Also, increasing leach rates (Table 2.12) appear to correlate with increasing iron oxide content, which is associated with a corresponding increase in residual glass and microcracking, both of which can affect the waste form's leachability. The leach rates of vitreous lab scale melts whose compositions ranged from A-0 to A-100 showed little dependence on silica or iron oxide content.[32] Based on analyses of leachants from the slag specimens, it was

found that the relative proportions of the leached components were similar for all samples and that Na, K, Si, and Al were preferentially leached. These constituents indicate that the glass phase is the major source of material leached. Two reasons have been offered for this conclusion:[23] (1) SEM/EDS results show that Na, K, Si, and Al have their greatest concentration in the glass phase, and (2) low concentrations of Fe, Mg, and Ca were found in the sample leachates. These elements are major constituents of the augite and spinel phases. The leach resistance of vitreous lab-scale basalt melts increased by almost two orders of magnitude when the Na_2O plus K_2O content was increased from about 5 to 14 wt %.[32] This emphasizes the effect of alkali content on glass phase durability and indicates the need to control the contribution of these constituents in the overall slag composition. The dependence of leach resistance of basalt glass ceramics on residual glass content has been discussed elsewhere.[33] Since the sodium content in the leachants was found to be relatively high, it is felt that its source may be from the glass and/or the crystalline phase. This claim is partially substantiated by leach data from PNL for basalt glass and basalt glass ceramics. The sodium leach resistance of basalt glass formulations did not greatly improve after intentional devitrification of these samples.[34] Thus, one explanation for the observed slag composition correlation with leach rates is that since the amount of residual glass in the A-series castings increased with decreasing silica content (or increasing iron content), it is possible that more glass is available for leaching.

As mentioned above, microcracking was found to increase with increasing iron content. This can lead to increased leachability due to (1) increased surface area available for leaching, (2) a high localized pH which can result in enhanced dissolution of Al_2O_3 and SiO_2, or (3) enhanced dissolution at crack tips due to high tensile stresses.[21,23] Lab scale slag preparations that underwent controlled cooling to produce either primarily vitreous samples or samples that were extensively devitrified did not display the extensive microcracking that was observed for the large scale castings.[24] In turn, the lab scale melts had leach rates about two orders of magnitude lower than the A-series specimens.[24,32]

To our knowledge, no data are yet available on the leach rates of transuranic radionuclides from IESB. Only qualitative information has been reported on the leachability of uranium from a glass whose composition was dictated by the relative proportions of the components leached from IESB.[24] Whether incorporation of transuranics into a UO_2-type phase (see Section 2.4.2.2) and/or a residual aluminosilicate glass phase in IESB will yield an acceptably leach resistant product is still open to question. A plutonium leach rate has been reported for a basalt glass made from Pu contaminated Hanford soil.[35] For a basalt glass sample containing 0.5 mg Pu/g of soil, the plutonium leach rates in deionized water [25°C, 98 d, powdered glass (based on information given earlier in reference 35)] were in the range 10^{-9}-10^{-8} g/cm^2-d. These leach rates are encouraging, in terms of IESB, since the Hanford glass contained 10 wt % each of B_2O_3 and Na_2CO_3, both of which can be detrimental to the glass' ability to resist chemical attack.

As far as the chemical durability of IESB is concerned, some additional observations and comments are given below. We feel that those areas of concern that are discussed should receive some attention in the further development of a durable IESB waste form.

(1) Earlier in this section, it was mentioned that the original SPI process for treatment of the TRU waste at INEL is undergoing additional review. This is because the resultant product from this process has a significant fraction of unoxidized metal and carbon. The presence of metal can affect a waste form's integrity due to the possibility of corrosion and nonuniformity of composition. Apparently, these problems are alleviated by the use of standard industrial melters common to the glass industry.

(2) It has been suggested that the leach resistance of the IESB basalt glass ceramic can be improved by limiting the residual glass phase content through controlled crystallization. However, the available data at this time do not totally support this claim. The leach rates of highly vitreous lab scale melts that had compositions simulating INEL low level TRU waste mixed with soil were found to be about two orders of magnitude less than the large scale slag specimens. The leach rate of a lab scale sample that was nearly completely devitrified, however, was not significantly different than for the vitreous samples. Similar behavior has been observed in the case of basalt glass/glass ceramic formulations containing simulated PW-9 waste calcine. The marginal improvement in leach resistance (about a factor of two) upon recrystallization led the author to conclude that there is no significant difference between the basalt glass and glass ceramic containing the waste calcine.[33] In another study, the leach rates (based on Cs and Sr) of certain devitrified Hanford basalt glass formulations were about 100-fold higher than those of the original glass.[25] In contrast to these results, preliminary data from PNL on the leach resistance of basalt glass and glass ceramic formulations for incorporation of blended transuranic process sludges and incinerator ash have shown that the chemical durability is improved by about an order of magnitude upon crystallization.[34]

Another point regarding achievement of high chemical durability in glass ceramics by minimizing the volume of residual glass was discussed in Reference 33. It was pointed out[33] that a large volume fraction of residual glass in basalt glass ceramics may be a desirable quality, especially for crystallization from a variable starting composition. With little or no control over the resultant glass phase that forms from a variable starting composition, it is felt that having a low volume of residual glass could lead to a poorly leach resistant product. A greater volume of glass will allow for incorporation of a larger fraction of leach resistant oxides (e.g., Al_2O_3, SiO_2, etc.). This is an important consideration for a waste stream as diverse in composition as the INEL TRU waste. Another point concerning devitrification is that crystallization may be undesirable in glass ceramics if the radionuclides concentrate in the

glass phase or at the crystal-glass phase boundary during crystallization.

It should be apparent that the exact manner in which crystalline phase formation affects the chemical durability of glass ceramics is not clearly understood. Why it is that devitrification improves the leach resistance of some glass ceramics and not others is open to question. Certainly, part of the answer lies in the composition of the parent glass and the crystalline phases that are eventually formed. Processing parameters may also be important factors. We feel that there is a need to understand the reason(s) for the discrepancy in leach behavior for basalt glass ceramics discussed above. Furthermore, it is essential that the behavior of transuranics (e.g., partitioning, solubility) in these glass ceramics be investigated. If the TRU elements partition mainly into the glass phase, then an additional nucleation and growth cycle may not be necessary in the fabrication of these waste forms but rather ways to improve the durability of the glass phase should be pursued.

(3) The role that iron plays in IESB appears to be fundamental to the integrity of this waste form. For example, a high iron content results in crust formation for the large scale castings, and the extent of microcracking is associated with a high iron content. In addition, the iron content is important to the chemical durability of the waste form, but exactly how this durability depends on iron content is not completely understood. For the A-series slag specimens, the leach rates clearly show an increase with increasing iron content.[23,32] For vitreous lab-scale melts that simulated typical INEL TRU waste, one report indicated that specimen leach rates were not a strong function of slag composition,[32] while another report stated that specimen leach rates were lower for the iron-rich slags.[31]

The Belgians have recognized the fact that, due to the variability in composition of TRU waste streams, it is important to understand the influence of the various constituents on the final properties of basalt-like waste forms.[28] With this in mind, they have initiated an experimental program that involves a structural investigation of the effects of incorporating large quantities of elements such as iron, copper, and aluminum in silica glasses. To date, they have only reported results on the incorporation of iron into a silica-glass network. As noted by the Belgian workers,[28] the behavior of iron ions in glass structures is far from being conclusive. The more important results of this work are summarized below.[26,28]

(a) Ferrous ions exhibited four-fold coordination only, while ferric ions exhibit both four-fold and six-fold coordination. The actual valence depended upon melting temperatures; higher temperatures favored Fe^{2+}. This is consistent with previous observations.[27]

(b) Apparently due to size effects, four-fold coordination in the Belgian glass formulations was limited to 50%.

(c) The amount of iron oxide that could be incorporated into the silica matrix depended on the cooling rate and, tentatively, the presence of certain alkali or alkaline earth oxides.

(d) Excess iron oxide (>20 mole %, water quenched samples) resulted in crystalline phase formation. This crystalline phase did not significantly affect the glasses' leach rate. This is consistent with some INEL leach data for a devitrified lab-scale specimen.[32]

(e) For a fixed alkali and alkaline earth oxide content, the leach rates of the glass specimens decreased with increasing concentrations of silicon and four-fold coordinated iron ions (about two orders of magnitude for the concentration range 66 to 72 mole %).

These results seem to suggest that a relatively large quantity of iron oxide can be contained in a basalt glass and that, because of the glass forming capacity, actually improves the overall durability of the glass. It is not clear at this time why a low iron content correlates with a low glass phase content in the A-series slag castings. The data from both Belgium and INEL would seem to indicate that some processing latitude exists with respect to iron content since a low iron content yields a low volume fraction of residual glass and a high iron content incorporated into an appropriately fabricated basalt glass both may result in a leach resistant product. Since the formation of the crystalline phases in basalt glass ceramic also depends on the oxidation state of iron which, in turn, is a function of the melt temperature, some compromise between cooling rate and melt temperature must be established in order to achieve the most durable product. While the work of the Belgians is certainly important to an understanding of the behavior of IESB, we feel that additional research in the area of compositional effects, including actinides, on the properties of IESB is warranted.

(4) Beall, et al. have identified a redox mechanism involving the Fe(II)/Fe(III) couple that is partially responsible for the sorption of actinides on various minerals.[36,37] By reducing the actinides to a lower, less soluble oxidation state, the dissolution and migration of the actinides are minimized. Based on this evidence, the divalent iron contained in basalt glass ceramics should be effective in preventing the oxidation of the transuranics in the waste form and inhibiting reactions with various complexes in the groundwater.

2.4.2.4 Radiation Stability

No concerted experimental effort is under way at INEL to study the effects of radiation damage on the stability of the IESB product. Some of the effects

of radiation damage include gross structural and microstructural changes (e.g., metamictization), changes in mechanical properties, and changes in leach rates. Because of the heterogeneous nature of TRU waste streams (including TRU element distribution), the variability in final product composition (glass and crystalline phases) and possible anisotropic distribution of the transuranics may lead to important radiation damage effects. The effect of alpha bombardment of non-actinide containing phases on product stability is another important consideration. While the anticipated actinide loadings in the waste forms are low (few tenths percent), the potential problem of radiation instability should not be dismissed out of hand based on inferential evidence. Actual waste-loaded full scale IESB products have not been fabricated. Thus, information on final phase characterization and actinide partitioning is lacking. Both are necessary in order to even speculate about the radiation stability of IESB. A more detailed discussion of radiation damage effects in TRU glass and crystalline waste forms is given in Section 2.9.

2.5 Specially Prepared Concretes

Three specially prepared concretes have been developed for nuclear waste immobilization. Of these, Mound Laboratory's cementitious pelletized waste form (CPWF) concrete has been applied specifically to TRU waste. The hot pressed concrete studied by Pennsylvania State University has not been studied with real or simulated TRU waste, nor with real or simulated waste spiked with TRU isotopes, so it cannot be evaluated as a TRU waste form. ORNL's FUETAP (Formed Under Elevated Temperature and Pressure) concrete, while developed particularly for HLW, has been spiked with realistic amounts of TRU isotopes and the leach resistance and radiolytic gas generation studied.

2.5.1 Cementitious Pelletized Waste Form Concrete

Mound Facility (MF) is responsible for the development and demonstration of a pelletized waste form for treatment and fixation of incinerator ash and process sludge generated at DOE sites. Other wastes considered for immobilization are bone char (used to sorb Pu) and salts generated from the aqueous off-gas scrubbing system of the MF cyclone drum incinerator. The various wastes are presently being immobilized by mixing with Portland cement and processing into pellets. This waste form has been referred to as cold-pressed concrete; however, in keeping with the nomenclature used by the Transuranic Waste Systems Office (TWSO),[38] it will be called Cementitious Pelletized Waste Form (CPWF) concrete in this report. The discussion that follows will deal with results on the incorporation of the following TRU contaminated waste streams into a waste-cement pellet formulation: (1) incinerator ash, (2) bone char, and (3) incinerator off-gas filter sludge. The waste form characterization studies conducted at MF included leachability, density, crush strength, mechanical strength, and waste loading. The information evaluated is from MF reports covering fiscal years 1978-1980 inclusive.

2.5.1.1 Pelletized Incinerator Ash-Cement Formulations

2.5.1.1.1 Physical and Mechanical Properties

A set of fixed processing parameters was chosen for preparation of the ash-cement pellets. The parameters which were held constant are:[39]

1. Pressing pressure of 173 MPa for 1-minute duration.

2. Three-gram matrix weight.

3. 1.3-cm pressing die, which, with a 3-g charge, produces a relatively standard 1.3-cm diameter by 1.3-cm high pellet [length/diameter (L/D) ratio approximately 1].

4. Dry Cure Cycle - two days (48 hr) in open atmosphere.

5. Wet Cure Cycle - four-day (96 hr) cure in distilled water followed by a two-day cure in open atmosphere.

Pellets were pressed with 60% (w/w), 65%, 70%, 80%, and 0% ash residue. The cement used in all formulations was Portland Type-IA. Four types of ash residue were used in the MF study. They differed according to the combustible stream fed into the incinerator. The elemental composition of sintered Type I incinerator ash is given in Table 2.13. The results of some physical and mechanical properties measurements for the various ash-cement formulations are summarized in Table 2.14.

The 65% dry-cured ash pellets produced acceptable crush strengths* for Types I, II, and III ash. For wet cured pellets, the 80% ash formulation was found to be best.[40] The free water content ranged from 0.22 to 1.2% (w/w) depending on the water/cement ratio and method of curing.[40] The compressive strength of the ash-cement pellets was found to increase with curing time. For the 65% ash-35% cement formulation (dry cured), the compressive strength increased from 24 MPa for two days of curing to 51 MPa for 95 weeks of curing.[41] The average compressive strength of pellets made from Pu-contaminated incinerator ash (65 wt%) that had been sintered for carbon removal was reported to be about 35 MPa.[42] Based on experiments that determined physical and mechanical properties, the incinerator ash waste loading will probably not exceed 70% (w/w). The overall process efficiency for the waste loading is reportedly a reduction in volume of uncompacted combustible waste of 99%.

The feasibility of incorporating LASL and SRP incinerator ash compositions into cement pellets was investigated.[43] Pellets incorporating ash compositions from MF, LASL, and SRP were prepared by mixing 65% (w/w) of the ash with Portland cement and then cold-pressing at 173 MPa for about one minute.

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*The established limit for acceptable compressive strength was quoted as 24 MPa (L/D = 1.0, 7 day, dry cure). No reference was given as to the origin or justification of this criterion.

Table 2.13

Elemental Content of Sintered Incinerator Ash
(This is Table 5 of Reference 39)

	Element (wt%)[a]																
Ash	B	Si	P	Al	Fe	Mn	Pb	Mg	Cr	Sn	Ni	Ca	Cu	Ag	Zn	Na	Ti
1-1	<0.05	17.8	0.05	17.8	2.5	0.06	0.04	3.0	0.30	<0.05	0.08	2.0	0.05	<0.05	3.0	0.35	3.0
1-2	<0.05	>5	<0.05	>5	3.0	0.05	--	1.5	0.10	--	0.08	2.5	0.10	--	1.0	0.25	1.5
1-3	<0.05	5.0	0.06	3.0	>5	0.10	--	1.0	0.30	<0.05	<0.05	>5	<0.05	--	0.15	0.30	>5

[a]Elemental analysis will not approach 100% because of volatile products of combustion, the method of determination, and oxide values.

Table 2.14

Pressed Ash-Cement Pellet Matrix Controlled Experimental Process
(This is Table 2 of Reference 40)

Ash Type	Ash Content (%)	Cement Content (%)	Water/ Cement	Cure		Average Weight Loss During Cure (%)	Density (g/cm^3)	Average Compressive Strength (psi)	Mechanical Shaking Weight Loss (%)
				Dry	Wet				
	0	100	0.10	X		5.9	2.29	3635	
	0	100	0.125	X		6.1	2.30	3661	
	0	100	0.15	X		6.5	2.32	3668	0.50
	0	100	0.175	X		6.7	2.33	3670	
	0	100	0.10		X	2.1	2.43	4580	
	0	100	0.125		X	2.0	2.45	4330	
	0	100	0.15		X	1.5	2.47	4192	0.84
	0	100	0.175		X	1.2	2.49	4293	
I	60	40	0.45	X		6.2	2.00	3470	4.45
I	60	40	0.45		X	4.1	2.30	3600	3.21
I	60	40	0.50	X		8.9	2.00	3470	0.62
I	60	40	0.50		X	3.5	2.29	3620	4.33
I	65	35	0.60	X		11.8	1.90	3484	
I	65	35	0.60		X	5.5	2.21	3583	
II	65	35	0.60	X		7.9	2.51	3605	
II	65	35	0.60		X	5.2	2.56	3911	
III	65	35	0.25	X		2.7	2.47	3618	
S-UK[a]	65	35	0.60	X		7.4	2.08	3619	
S-UK[a]	65	35	0.60		X	3.3	2.18	3733	
I	70	30	0.70	X		11.0	1.96	2480	1.78
I	70	30	0.70		X	4.9	2.01	3640	3.70
I	70	30	0.75	X		11.1	1.96	3470	2.27
I	70	30	0.75		X	3.2	2.11	3625	3.63
I	80	20	1.10	X		7.1	1.92	2480	3.72
I	80	20	1.10		X	3.3	2.08	3600	3.84
I	80	20	1.15	X		7.9	1.92	2480	1.85
I	80	20	1.15		X	2.9	2.08	3570	4.45
I	80	20	0.70	X		9.0	2.03	~2507	
I	80	20	0.70		X	2.7	2.15	~3640	
I	80	20	0.85	X		9.0	2.04	~2500	
I	80	20	0.85		X	5.6	2.10	~3670	

[a]S-UK - denotes pellets containing 3 wt% Na_2SiO_3 and were made with "unknown" type ash.

The compressive strength of these ash-cement compositions was then determined as a function of the L/D ratio of the pellet. In all cases, the compressive strength decreased with increasing L/D ratio. The MF and SRP ash-cement composition had acceptable compressive strength values for L/D ratios of 1.0 and lower. Pellets incorporating LASL ash had relatively low strengths. Additives and increased manufacturing pressures resulted in increased strength but at the expense of lower ash loading (25-35%, w/w).

2.5.1.1.2 Chemical Durability

The results of early leach tests[44] on Pu-238 doped ash-cement pellets have been discussed.[45] Since that time, more data have been published.

Leach tests have been conducted on Pu-238 doped 65% ash-35% cement pellets (1.3-cm diameter by 1.3-cm high) at ambient and 70°C in saturated NaCl brine solution and deionized water. The pellets were loaded with 0.25 wt% Pu-238 oxide (~0.13 Ci). This is significantly higher than the expected contamination level from actual waste processing. The higher plutonium doping levels were required by the leachate analysis techniques. Two leach test procedures were used: (1) Interim TRU Waste Leach test for WIPP,* and (2) ANS 16.1. For the first procedure, pellets were suspended by a nylon string in the leachant. After leaching for a prescribed time period (unknown), the pellet was removed from the solution and placed into fresh leachant. Incremental plutonium leach rates were determined from the fraction of PuO_2 leached, mass of the pellet divided by the geometrical surface area, and the reciprocal of the leach period.

Preliminary results indicate that the plutonium leach rate steadily decreases with time in brine solution at 22°C.[46] After 100 days of leaching, the leach rate decreased to less than 10^{-10} g/cm^2-d. However, from 120 days to 180 days, the leach rate was observed to steadily increase. The average leach rate for pellets suspended in brine solution at 70°C is 2.6×10^{-8} g/cm^2-d.[46] These results are in contrast to an earlier report that indicated the plutonium leach rate in brine was greater at ambient than at 70°C.[47] However, these data were for tests conducted for only 50 days. Apparently, the pellets used in the 70°C brine leach tests, or ones just like them, broke apart after 75-99 days of leaching.[46] Problems in the manufacture of the original pellets for the 70°C brine leachant tests might account for the non-Arrhenius behavior originally reported. It has recently been reported that leach tests of the ash-cement pellets in brine at 70°C proved to be inconclusive because of scatter in the data.[48] However, these results were for pellets that did not meet some of the MF screening criteria.** Data apparently are available for pellets that have been leach tested in 70°C brine for at least 14 months.

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*Reference to this procedure has been made elsewhere,[3] but the final version apparently has not been published.

**J. W. Doty, Mound Facility, private communication to G. Bida, BNL, June 11, 1981.

The plutonium leach rates for the ash-cement pellets in deionized water at 22°C were found to be cyclic with time and, after 140 days of leaching, were in the range 10^{-7} - 10^{-6} g/cm^2-d.[46] These Pu-238 leach rates are about five orders of magnitude greater than those for brine. Some experimental difficulties were encountered during leachate analysis of these samples.* We understand that more recent long term leach data for pellets in deionized water are in accord with normal leaching behavior and that the difference in plutonium leachability for brine solution versus deionized water is roughly a factor of 40. No results were reported for leach tests in deionized water at 70°C at this time. Leach tests using the two different test procedures were performed on ash-cement pellets in deionized water at ambient temperature. Test results for the first 180 days were in good agreement with rates in the range 10^{-7} -10^{-6} g/cm^2-d.[48] As noted in reference 46, this result was expected since the procedures are almost identical except for leachate sampling frequency. Additional long-term leach tests are reportedly planned for both ash-cement and sludge-cement formulations.[46,48] Comments on the compliance of this waste-cement formulation with the adopted 10^{-5}/yr actinide release rate criterion will be reserved until Section 2.5.1.4.

2.5.1.2 Pelletized Sludge-Cement Formulations

Experiments were conducted at MF on the fabrication of sludge-cement pelletized waste forms using simulated and Pu-238 contaminated incinerator off-gas sludge. The data reported included simulated and "hot" sludge characteristics, sludge loading percentages for the sludge-cement matrices, effect of additives on strengths and handling characteristics, and optimum water/cement ratios for sludge-cement pellets.

2.5.1.2.1 Physical and Mechanical Properties

The chemical composition of the simulated sludge was determined. The wet sludge contained approximately 70% water and 30% solids. The composition of the calcined (800°C) sludge is given in Table 2.15 below.

The results of experiments[43] performed to evaluate the effect of various parameters on the compressive strength of sludge-cement pellets are summarized below:

(1) The optimum water/cement ratio (that of the sludge-cement mixture before pressing) was found to be 1.6 for 50% sludge-50% Portland cement pellets.

(2) Addition of about 7% (w/w) sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$) to 60% (w/w) sludge increased the compressive strength to the acceptance level.

(3) Doubling the pellet manufacturing pressure (to 346 MPa) increased the average crush strength 25 to 41% depending upon pellet composition.

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*J. W. Doty, Mound Facility, private communication to G. Bida, BNL, June 11, 1981.

Table 2.15

Chemical Composition of Simulated Sludge After Calcining at 800°C
(Data from Table 3 of Reference 43)

Element or Ion	Amount Present (wt %)
Na	14.8
Al	15.9
Si	15.5
Ti	2.0
Zn	2.0
Fe	1.0
Pb	0.8
Ca	0.9
Mg	0.3
F^-	0.01
Cl^-	1.40
$SO_4^=$	0.75
C	0.08
O_2	remainder

(4) The compressive strength of 50% sludge-50% high alumina cement (HAC) is about 32% greater than for the same sludge-Portland cement composition.

(5) Additives (other than sodium metasilicate) investigated for effect on compressive strength included NaOH, CaO, $CaCl_2$, Al_2O_3, MgO, SiO_2, K_2SiO_3, Micro-Cel (synthetic, hydrous calcium silicate), and Celite (amorphous silica). Only addition of 5% NaOH resulted in a significant increase (~166%) in crush strength.

Sludge containing a small concentration of Pu-238 oxide was used in the processing of sludge-cement pellets.[47] The raw wet sludge contains ~73% water and 27% solids. For pellet manufacturing, the sludge is calcined at 700-800°C for three hours which results in nearly complete (99.6%) removal of carbon. The chemical composition of this "hot" calcined sludge is given in Table 2.16. The major constituents are sodium, iron, and silicon. Aluminum was more abundant than iron for the simulated sludge.

The effects of the following variables on the compressive strength of the sludge-cement pellets were determined: sludge content, water/cement ratio, manufacturing pressure, and additives ($Na_2SiO_3 \cdot 5H_2O$, CaO, $CaCl_2$, and NaOH). For pellets of similar weight percent composition and fabrication parameters, a marked increase in compressive strength was noted for "hot"

Table 2.16

Chemical Composition of Calcined Sludge
(Data from Table 5 of Reference 47)

Element	Amount Present (wt %)
Na	>6.0
Fe	>6.0
Si	>6.0
Ca	>2.0
Al	>0.8
Cr	>0.8
Zn	0.6
Pb	0.5
Ni	0.5
Ti	>0.5
Mg	0.4
Sb	0.4
Cu	0.2
Mn	0.1
C	0.1

sludge-cement pellets versus simulated sludge-cement pellets. The only variable that had a significant effect on compressive strength was the additive sodium metasilicate. All pellets containing $Na_2SiO_3 \cdot 5H_2O$ had strengths <3500 psi. This is in contrast to the behavior for simulated sludge-cement pellets.

2.5.1.2.2 Chemical Durability

Leach tests were conducted on Pu-238 doped 50% sludge-50% cement pellets (1.3-cm diameter by 1.3-cm high) at ambient and 70°C in saturated brine solution. No data have been found for leaching in deionized water. The same test methods were used as for the ash-cement pellets. The plutonium leach rate decreased to about 10^{-10} g/cm^2-d after 120 days of leaching.[48] From 120 to 250 days, the leach rate has been slowly increasing but is still in the range 10^{-10} -10^{-9} g/cm^2-d.[48] The leach rate is insensitive to temperature in the range of ambient to 70°C.[48] Unlike the ash-cement pellets, the sludge-cement pellets appear to have a surface layer of crystals.[46] It is felt that this layer may partially account for the lower leachability of the sludge-cement pellets.

2.5.1.3 Pelletized Bone Char-Cement Formulations

2.5.1.3.1 Physical and Mechanical Properties

Bone char, calcium hydroxyapatite [$Ca_5(PO_4)_3(OH)$], is routinely used at MF as a liquid adsorbent. As such, it can become contaminated with >10 nCi/g

of plutonium and require safe disposal. This material has also received some attention as a waste stream that might be incorporated into a pressed cement matrix.

Bone char-cement formulations have not been studied as extensively as the ash- and sludge-cement formulations. Thus, we only briefly summarize the pertinent data here.[42] Several pellets were prepared using various ratios of bone char to cement and then either dry-cured or wet-cured. No details of curing methods were given. The densities of the dry-cured pellets increased with decreasing bone char content and were in the range 2.1 - 2.2 g/cm^3. The crush strength reached a maximum of 44 MPa for the 70% char-30% cement cry-cured formulation. The densities of wet-cured pellets also increased with decreasing bone char content and were about 2% higher than dry-cured pellets. The compressive strength of the wet-cured 70% bone char-30% cement matrix is 90 MPa. The 70/30 mixture was judged best for the bone char-cement matrix based on compressive strength.

2.5.1.3.2 Chemical Durability

To our knowledge, no plutonium leach rate data have been reported for bone char-cement pellets. Bulk matrix dissolution rates as determined by weight loss measurements have been reported.[44] These dissolution rates are of the order of 10^{-4} g/cm^2-d.

2.5.1.4 Compliance with Release Rate Criterion

In general, the limited data available for the plutonium leachability of the waste/cement pellets appear promising in terms of the 1 part in 10^5/yr release rate criterion. For the pellet dimensions given and using the geometrical surface area, the leach rate must be $\leq 10^{-8}$ g/cm^2-d to meet this requirement. However, the existing leach data for these waste forms are incomplete and, in certain instances, inconclusive. We have learned that the pellet dimensions for actual waste disposal will be 2.54-cm diameter by 2.54-cm high.* No data appear available on the leachability of plutonium from pellets of these dimensions. More importantly, these pellets will be placed into a can large enough to accommodate 50-100 pellets. Some of these cans will in turn be placed into a 210-L drum. It seems worthwhile to investigate if, and how, the leachability of such a configuration as fifty or so pellets in a container differs from that of fifty individual pellets. Some additional comments on the chemical durability of these waste forms are given below:

(1) The waste forms discussed herein have been described as high density, low porosity pellets.[41] However, it is interesting to note that cold pressed pellets prepared at MF had sorbed as much as 16 wt% water after submersion.[49] Also, surface area measurements (we assume via gas adsorption methods) on pressed ash-concrete pellets of

*E. L. Lewis, Mound Facility, private communication to G. Bida, BNL, June 5, 1981.

slightly different dimensions than discussed above yield areas that are some four orders of magnitude larger than the geometric surface areas,[41] indicating that the waste-cement pellets are rather porous. In calculating plutonium leach rates, geometric surface areas have been used.[47,48] Realistically speaking, the effective waste form surface area contacted by the leachant will lie somewhere between the geometric surface area and the experimentally measured surface area. The actual plutonium leach rates will, of course, be lower than what has been reported and discussed above. However, in the interest of valid intercomparisons with the leachability of other TRU waste forms, the extent of porosity should be determined and the "effective" surface area should be better defined.

(2) The matrix dissolution rate for a pellet comprised of 60% ash-40% cement and fabricated in a manner similar to that described above was reported to be $\sim 1.5 \times 10^{-4}$ g/cm^2-d in distilled water, presumably at ambient temperature.[50] For ash-cement pellets doped with Pu-238, the leach rates in distilled water were found to be a function of percent ash in the pellet. In the case of a 60% ash-40% cement composition, the average Pu-238 leach rate was found to be 3.8×10^{-10} g/cm^2-d.[44] Ignoring differences in pellet weight, size, manufacturing pressure, etc., this is about what would be expected based on the original weight of Pu-238 in the pellet and assuming congruent dissolution. Such data do not appear to be available for sludge-cement pellet formulations. If congruent dissolution is occurring, it may be related to the concrete's porosity. It is also possible that the porous nature of these pellets could lead to enhanced dissolution over long time periods due to a relatively rapid breakdown of the matrix structure. On the other hand, corrosion products may build up within the interstices of the concrete and suppress dissolution. The behavior of ash-cement pellets in brine solution after 120 days of leaching suggests that a better understanding of the leaching mechanism of CPWF concrete and factors affecting the mechanism are in order.

(3) A final point that should not be overlooked is that the plutonium leach rates reported for CPWF concrete pellets are for samples spiked with a much larger quantity of TRU than will actually be incorporated in these pellets. Although variations are expected in the weight percent of transurancics in the waste streams, normal operations at MF result in contamination levels that are about one to two orders of magnitude lower than the dopant level required for leach testing.

2.5.2 FUETAP Concrete

Oak Ridge National Laboratory (ORNL) has developed FUETAP concrete particularly for immobilization of HLW, using simulated SRP wastes. As part of their program, radiolytic gas generation has been studied by doping samples with relatively large amounts of TRU isotopes, especially Cm-244, in order to obtain

in a short time the alpha radiation dose which would be delivered to an actual waste form in thousands of years. Plutonium leach rates have been determined for doped specimens containing simulated HLW, and it is planned to repeat the tests using actual TRU waste.

2.5.2.1 Preparation and Properties

The standard FUETAP formulation is given in Table 2.17.[51] Up to 25 wt % simulated waste can generally be incorporated. The compositions of three of those which have been used are given in Table 2.18.[51] In order to make pourable grouts with SRL 2, small changes had to be made in the standard formulation, such as increasing the water content from 15 to 18% to satisfy the high water demand of the zeolite.

The original curing conditions for FUETAP were 250°C and 4.1 MPa for 1.5 hours.[52] As development proceeded and investigations of the effects of changes in the earlier formulation gradually led to the choice of the mix given in Table 2.17, it was found that high quality concrete was produced with very much milder curing conditions. With 24 hours curing at 100°C and a pressure 0.1 MPa above atmospheric, specimens were prepared with compressive strengths essentially the same as those of specimens prepared under the previous

Table 2.17

Standard FUETAP Formulation

Ingredient	wt %
Type I Cement	22.00
Kingston Fly Ash	11.00
Indian Red Clay	7.50
Simulated Waste	15.00
Sand	27.75
$NaNO_3$	0.75
D-65 (Water Reducer)	1.00
Water	15.00

conditions.[51] The compressive strengths of cured specimens are generally about 60 MPa, the density around 2.0 g/cm^3, and thermal conductivity 1.0 W/m-K.[53]

Dewatering of the cured concrete is carried out to remove unbound water so as to avoid as much as possible the generation of gas by water radiolysis when actual radioactive waste is incorporated. The dewatering is accomplished by heating at 250°C for 24 hours. Under these conditions, there is approximately 13% weight loss, and about 2 wt % unbound water is calculated to remain.[51] Compressive strength is reduced about 20%, which brings it into the range of high-strength commercial concretes.

Table 2.18

Composition of Simulated Waste Solids

Component	NFS (Wt %)	SRL1 (Wt %)	SRL2[a] (Wt %)
Fe_2O_3	75.18	38.4	36.13
Al_2O_3	14.89	6.8	28.26
MnO_2	--	17.1	9.94
PbO[b]	--	16.5	3.26
CaO	--	1.0	2.69
NiO	4.78	6.5	4.47
Cr_2O_3	4.94	0.5	--
Na_2O	--	--	5.08
Na_2SO_4	--	--	0.93
$Na_2SO_4 \cdot 10H_2O$	--	7.0	--
NaF	--	2.0	--
Na_2HPO_4	--	1.4	--
SrO	0.14	--	--
$Ru(OH)_3$	0.027	--	--
CeO_2	0.037	2.5	--
BaO_2	--	0.3	--
SiO_2	--	--	0.85
Zeolite[c]	--	--	8.93

[a] Values taken from J. A. Stone, S. T. Goforth, Jr., and P. K. Smith, Preliminary Evaluation of Alternative Forms for Immobilization of Savannah River Plant High-Level Waste, DP-1545, December 1979.

[b] PbO substituted for U_3O_8.

[c] Ion-Siv 1E-95.

2.5.2.2 Radiolytic Gas Generation

Generation of gas by radiolysis of the water in concretes is a well known effect. ORNL has determined in a laboratory study[54] that hydrogen and oxygen combined catalytically in the presence of FUETAP without any added radioisotopes, at a much higher rate than occurred with regular hydraulic cements. The combination rate was equivalent to the hydrogen production rate which would be expected in concrete subjected to an internal dose rate of about

10^6 rad/hr, assuming a hydrogen yield of 0.5 molecules/100 ev. On this basis, ORNL felt that little or no gas should form in FUETAP concrete containing radioisotopes producing such a dose rate.

In studies done at SRL,[49,55] however, production of oxygen from radiolysis of water in concrete was found to be generally less than stoichiometric and often nearly zero. Thus, as pointed out by BNL,[56] the fact that hydrogen and oxygen combine stoichiometrically in the presence of FUETAP would be of no help in preventing gas build-up if little or no oxygen were formed with which hydrogen could recombine. Also, because of the fire and explosion hazards from hydrogen build-up in a repository, it is essential to know whether and to what extent hydrogen would form in FUETAP loaded with actual waste.

In order to determine the extent of gas generation in FUETAP, ORNL prepared two concrete specimens containing 0.4 mg Cm-244/g concrete, one cured under standard FUETAP conditions, and then dewatered, the other cured under ambient temperature and pressure.[53] After 5 months, the gas generation rate from the FUETAP specimen was approximately 1/20 that from the regular hydraulic cement specimen.[57] The composition of the gas was not determined in either case. In discussions with ORNL,* it was determined that they intended to analyze the gas formed in these experiments when the pressure build-up phase was terminated. It was expected that it would be largely hydrogen.

It was indicated by ORNL that the results of their long-term gas generation study confirmed the fact that the generation rate in FUETAP was very low--so low that it would cause no problems even if it were all hydrogen. For a 200-L drum 90% filled with FUETAP, the maximum pressure developed in the equivalent of 5×10^4 years for a realistic actual waste loading would be 0.2 MPa. This result was obtained using a dose rate some 10^4 times that expected in actual waste, but the dose rate effect is such that lower dose rates give lower radiation yields. Thus when the dose rate effect is taken into account, it is probable that even lower pressures would be obtained in the long term storage situation.

2.5.2.3 Leach Resistance

All the leaching studies reported to date have been done with samples containing HLW, and the emphasis has been on determining the behavior of fission product and matrix elements. However, the leach rate of plutonium has been determined at 25°C using quartz distilled water leachant in a modified IAEA test in which the leachant was changed daily.** From 3 to 56 days, the leach rate remained essentially constant at approximately 10^{-6} g/cm^2-d. ORNL plans to

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*L. Dole, Oak Ridge National Laboratory, private communication with D. MacKenzie, BNL, May 5, 1981.

**J. G. Moore, Oak Ridge National Laboratory, "Program Review of FUETAP Concrete," presented at the DOE High-Level Waste Technical Review, Atlanta, GA, May 18-19, 1981.

determine the Pu leach rate from samples containing actual TRU waste, but until this is done, no conclusion can be drawn on the usefulness of FUETAP concrete for incorporation of TRU wastes. At this stage, all that can be said is that the Pu leach rate from the ORNL sample containing simulated HLW was somewhat higher than that determined at BNL from regular hydraulic cement samples containing actual TRU waste.

2.6 Pacific Northwest Laboratory/TRU Waste Immobilization Program

A major effort in the area of development and characterization of TRU waste forms was initiated at Pacific Northwest Laboratory through the Transuranic Waste Systems Office. This effort has been directed at immobilization of the two categories of TRU waste that do not meet the present waste acceptance criteria for WIPP, i.e., incinerator ash and process sludge. Several waste forms have been chosen for evaluation according to a set of standard waste form characterization tests. This evaluation is part of a comparative assessment of alternative immobilization technologies for selected TRU wastes. Our review of the PNL program will cover material reported mainly in quarterly progress reports up to the end of FY 80. Some additional work on development of a borosilicate glass for incorporation of RFP TRU incinerator ash, originally discussed in the Interim report,[45] will also be included. In addition to the material detailed in their progress reports, we obtained a useful persepective of the PNL efforts through several discussions and a meeting[58] with the personnel involved in the Transuranic Waste Immobilization Program. Information gathered from these discussions will be included in the evaluation that follows.

2.6.1 Objectives and Scope of PNL Program

The purpose of this section is to outline the activities of the TRU Waste Immobilization Program (TRUWIP) and to make clear the intent of the program during the present and previous fiscal years. A two-year comparative assessment study of alternative immobilization systems for selected transuranic wastes was initiated at the start of FY 80. The second phase of TRUWIP had as its objectives the development and characterization of the most promising waste form(s) resulting from the comparative assessment and bench- and pilot-scale development of the fabrication process for the selected system(s). This program was designed to continue at least through the end of FY 86. The overall program consists of several tasks; however, some of these will not be discussed in detail except where they may be of importance to waste form development. Such tasks include systems analysis activities designed to adapt multi-attribute decision theory for rank ordering the alternative systems and a process evaluation and cost estimate task that has reviewed several process alternatives that could be implemented for the reference waste.

An initial set of about 40 candidate immobilization systems was screened according to criteria in the form of process and product objectives and requirements.[59] This set was further reduced according to compliance with certain immobilization system objectives and screening criteria.[59] The objectives and criteria for screening waste products included: (1) $\geq$20 wt % design waste loading, (2) matrix leach rate $\leq 10^{-3}$ g/cm^2-d (static, deionized

water, 28 days, ambient), (3) waste form volume ≥ 0.07 cm^3, (4) respirable fines on impact ≤ 1 wt %, (5) macroscopic homogeneity not required, and (6) product must meet all minimum standards with all waste variants defined. At this time, the waste forms that have been selected for the comparative assessment study are: (1) cast hydraulic cement, (2) cold-pressed hydraulic cement, (3) borosilicate glass, (4) aluminosilicate glass, (5) basalt glass ceramic, and (6) sintered silicate ceramic. We are not sure if normal cast concrete is indeed a serious waste form candidate or if it has been included for comparative purposes, as suggested elsewhere.[38] Certainly, economics has played an important role in the choice of some of the candidates while others were chosen based on information gained from PNL's Alternative Waste Forms Program for HLW immobilization. The next phase in the assessment study is to perform some waste form scoping experiments designed to improve the performance of some of the candidate products. Finally, as part of the immobilization technologies assessment profile, the candidate waste forms will be subjected to standard waste form characterization tests. The standard tests are to include:[58] (1) static tensile strength, (2) impact behavior, (3) bulk and actinide leaching behavior via MCC-1 procedures (to include leachate and surface analysis), (4) sensitivity of leaching behavior to variations in the chemical/physical properties of the waste or additives (judged to be one of the most important properties in need of thorough understanding), and (5) bulk properties (density, elemental analysis, surface and microstructural analyses, etc.), and an assessment of radiation stability. This information will be used in the overall evaluation scheme, which includes several evaluation attributes (e.g., relative costs, safety considerations, etc.), resulting in the selection of the most promising waste product/process for further development and demonstration.

The scope of the PNL TRUWIP is certainly commendable in terms of the kind of information that it will generate and which is necessary for NRC licensing purposes. Whether the information provided will satisfy the adopted 10^{-5}/year release rate criterion for TRU waste forms or other NRC requirements is an open question. This will depend, in part, on general acceptance of the standard test methods used in the waste form evaluation. Although at one time the intent of DOE was "...to achieve the ideal condition where the release rate requirement could be totally assumed by the waste form...,"[38] the incentive to do so is lacking for, at least, two reasons: (1) the present wording of 10 CFR 60,[1] and (2) the decision to dispose of the existing TRU inventory in WIPP. Regardless, the concerted effort on the part of PNL to conduct such a comprehensive evaluation of immobilization systems for even a small fraction of the TRU waste volume is noteworthy. A valid intercomparison of the performance of the various waste forms will be possible because of the use of standard (or, at least, uniform) test methods. It is our understanding that due to the WIPP decision, the TRU Waste Immobilization Program at PNL will be severely curtailed. However, it is their intent to complete the comparative assessment study by the end of FY 81.*

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*W. A. Ross, Pacific Northwest Laboratory, private communication to G. Bida, BNL, March 24, 1981.

For the purpose of this evaluation, the results of the comparative assessment study of FY 80 will be discussed. Since this is the first year of that program, detailed experimental results are limited. Accomplishments during this first year include: (1) characterization and selection of a reference TRU waste, (2) identification of the waste form alternatives, (3) scoping experiments designed to improve and understand the behavior of some promising waste forms, and (4) preparation of the waste forms using the reference waste for the comparative study. Because of the evolutionary nature of the first part of the PNL program, we have chosen to present the data on the waste forms in the chronological order in which they were reported. We will then return to some earlier work on the incorporation of TRU incinerator ash into borosilicate glass, a generic solubility study for TRU waste oxides in borosilicate glass, and a scoping study on the feasibility of fabricating sintered silicate ceramics from selected TRU wastes.

2.6.2 Characterization and Selection of the Reference TRU Waste

Prior to the review of the TRU waste forms effort at PNL, it is worthwhile to discuss the results of the waste characterization task of the comparative assessment program. As part of the standard test methodologies approach for evaluation of the selected immobilization systems, waste forms will be fabricated from a given weight fraction of a reference waste. This reference waste is a blend of sludge and ash that has been developed using Rocky Flats Plant production facilities as a model.[59] Process sludge and incinerator ash were chosen for study because of their importance in the TRU waste inventory and because they do not comply with WIPP waste acceptance criteria.[4] First- and second-stage sludges comprise 9% of the TRU waste volume and 14% (w/w) of the total plutonium inventory in retrievable storage at INEL.[60] Leached incinerator residues are a minor component of the inventory but constitute 8% (w/w) of the plutonium. It should be noted that the blended waste is for reference purposes only. It is hoped that the selected immobilization product/process will accept a wide variation in waste stream. In fact, the purpose of the waste characterization task was to determine the variation to be expected in the two waste residues. This information is essential in establishing flexibility requirements for candidate waste forms and in formulating guidelines for determining the sensitivity in waste form properties to these variations in the waste.

Transuranic contaminated process sludges are generated mainly at Rocky Flats Plant and Los Alamos Scientific Laboratory from research and defense-related production activities. Details of the chemical processes that generate these sludges are given elsewhere.[60] A sampling and analytical program to determine the compositional variability of the actual sludges was initiated by PNL in cooperation with RFP and LASL. A variety of wet chemical and instrumental techniques were used to analyze for cations and anions in excess of 1% (w/w). Residual water content and Pu, Am, and U concentrations were also determined. Analytical techniques included emission spectroscopy, atomic absorption spectrometry, x-ray fluorescence, and other spectrophotometric, gravimetric, and titrimetric methods. Analyses were conducted

for six RFP sludge samples and four LASL samples. The results are listed in Tables 2.19 and 2.20. The major constituents in both sludge types are Ca, Fe, and Si, while Na is a major constituent in the RFP sludge only. This is due to a difference in the treatment of ion-exchange effluents at the two sites. A high carbonate content is noted for the LASL sludge and this is due to the treatment of lime (used for pH adjustment) with CO_2.

The properties of incinerator ash residue were also determined. Incineration of contaminated combustible waste is being developed at several DOE facilities.[61] At Rocky Flats, a production scale rotary kiln incinerator and a pilot-scale fluidized bed incinerator have been undergoing development for the purposes of plutonium recovery and volume reduction. By analyzing the nonvoltaile, inorganic components of several combustible materials (e.g., paper, PVC, wood, etc.), a data base was available for use in the computer simulation of the ash composition that would result from incineration of any hypothetical combustible mixture. Actual TRU contaminated ash from an operating incinerator is not available. The average ash composition of 46 such simulations are given in Table 2.21. As noted elsewhere,[60] ash compositions may be encountered that are vastly different than that listed in Table 2.21. However, these values provide the best estimate based on currently available information. It is noted that the ash is high in alumina, silica, and titania content. Also, the PbO content is quite high and rather variable.

Based on waste generation information from RFP, the ratio of sludge production to incinerator ash production will be about 3:1. Thus, a blend of sludge and ash in this ratio has been chosen as the reference blend for the comparative assessment study. Nonradioactive sludge and ash were obtained from RFP, duplicating actual production wastes as closely as possible. To these wastes, reagents were added to bring the mix of sludge and ash to the compositions given by the flowsheets for sludge and by the incinerator simulation for ash. The reference blended sludge-ash composition is given in Table 2.22. Conclusions from this study of the characteristics of transuranic solid waste residues are as follows:[60]

(1) For incinerator ash, large variations in the chemical composition may be expected if the feed is not homogenized. An example is the high lead content that can result from combustion of glove-box gloves. Ash of such a high lead content may require separate treatment, depending on waste form.

(2) Sludge analyses indicated variation in some metallic constituents for a given site (mainly RFP) and significant variations in Ca, Na, and Al between sites.

(3) Carbonate anion is a major constituent of LASL sludge.

(4) The transuranic content of sludge is low for both LASL and RFP. The assumed incinerator ash contamination (0.2 wt % plutonium[59]) is somewhat higher but, because of the sludge to ash mixing ratio, the

Table 2.19

Rocky Flats Plant Sludge Analysis
(This is Table 4 of Reference 60)

Constituents Analyzed	Average, wt %	Range, Wt % High	Range, Wt % Low
Al	0.9	2.0	0.5
Ca	9.9	19.4	3.8
Fe	5.0	5.2	4.0
K	1.7	6.5	0.6
Mg	4.2	10.0	1.0
Na	10.0	14.0	6.6
Si	7.8	10.0	5.0
NO_3^-	7.4	9.1	4.2
PO_4^{-3}	3.2	8.9	0
CO_3^{-2}	1.7	5.1	0.4
SO_4^{-2}	0.3	0.4	0.2
Cl^-	0.6	0.8	0.2
F^-	0	0	0
H_2O	50.5	61.0	19.4
Pu (ppm)	16	39	4
Am (ppm)	8	32	1
U (ppm)	410	1700	1

Table 2.20

Los Alamos National Laboratory Sludge Analysis
(This is Table 5 of Reference 60)

Constituents Analyzed	Average, wt %	Range, wt % High	Range, wt % Low
Al	0.4	0.4	0.3
Ca	7.1	7.7	6.0
Fe	1.0	1.2	0.8
K	<0.3	<0.3	<0.3
Mg	0.3	0.3	0.3
Na	<0.3	<0.3	<0.3
Si	2.9	3.9	2.3
NO_3^-	0.4	0.8	0
PO_4^{-3}	0.9	1.5	0.4
CO_3^{-2}	10.0	11.5	8.1
SO_4^{-2}	0	0.1	0
Cl^-	0	0	0
F^-	0.1	0.1	0.1
H_2O	70.1	71.6	67.5
Pu (ppm)	1	2	1
Am (ppm)	0.1	0.1	0.1
U (ppm)	81	104	69

Table 2.21

Chemical Composition of Typical Incinerator Residues Based on 46 Simulations (This is Table 9 of Reference 60)

Compound	Composition, wt %			
	Average	Std. Dev.	Low	High
Al_2O_3	15	4.5	2.0	20.1
BaO	0.8	0.6	0.3	3.1
CaO	3.3	1.1	1.7	8.2
Fe_2O_3	0.4	0.1	0.2	0.9
K_2O	0.8	0.3	0.3	1.6
MgO	4.4	1.9	0.6	10.9
Na_2O	1.5	1.0	0.6	4.0
PbO	8.0	16.0	0.1	61.7
SiO_2	21.0	5.0	4.0	27.0
TiO_2	20.0	7.0	2.5	29.0
ZnO	1.0	1.0	0.5	2.4
C	8.0	4.0	3.6	21.9
S	0.3	0.2	0.1	0.9
P_2O_5	5.0	5.0	0.4	25.2
Other	11.0	1.0	9.3	14.4

Table 2.22

TRU Reference Blended Waste
(Data from Table 10 of Reference 60)

Blended Waste 3:1 Sludge/Ash:	Weight Percent									
	Al	Ca	Fe	K	Mg	Na	Si	P	Ti	H_2O
Calculated	2.1	3.2	9.8	1.9	0.9	4.8	14.0	1.4	3.0	7.5
Actual	3.0	4.6	9.1	1.2	2.0	3.0	15.5	1.9	3.6	7.5[a]

[a] Indicates calculated value.

actinide content should be on the order of a few hundredths weight percent.

2.6.3 Comparative Assessment Study

One accomplishment of the TRUWIP during FY 80 was the selection of the six immobilization systems that will undergo further characterization and testing. These were identified earlier. One of the waste form candidates is sintered silicate ceramic. Results of a scoping study on silicate ceramic for TRU waste immobilization conducted during an earlier phase of the PNL program will be discussed below. Ceramic pellets were prepared by ball milling a mixture of 67 wt % reagent grade bentonite and 33 wt % TRU blended waste (TBW), cold pressing at pressures from 32 to 1600 MPa, and sintering at 1000°C for 8 hr.[29] The blended waste used in the preparation of these pellets was a mixture of process sludge and ash from a controlled air incinerator in a 9:1 weight ratio. Sintered pellet densities were observed to decrease with increasing compaction pressure. Also, because of crack formation above 124 MPa, it was decided that additional pellet compaction would be done at 62 MPa. In another set of scoping experiments for silicate ceramic,[62] pellets were prepared by ball milling a mixture (2:1 by weight) of bentonite and other clay minerals with TRU blended waste (3:1 blend, hereafter designated TBW-R), pressing at 124 MPa and sintering for 2-12 hr at 900-1100°C. These pellets were to be subjected to density measurements and static leach tests to determine optimum sintering conditions. A third variation of pellet preparation has been reported:[34] 67 wt % bentonite plus 33 wt % TBW-R ball milled for 5 hr, pressed at 69 MPa, and sintered in air at 1000°C for 2 hr. These pellets are to be evaluated in static leach and mechanical properties tests during FY 81.

Cementitious waste forms are being fabricated at PNL by a technique similar to the cold pressed pellet method developed at Mound Facility (see Section 2.5). Pellets pressed at 159 MPa were found to contain ~10 wt % water.[29] After curing, the Mound pellets contain 2-4 wt % water. A low water content is important in terms of gas generation potential (see Section 4.4.2.3). Higher compaction pressures resulted in denser pellets. However, a more dense pellet means that, because less water is available for hydration, inferior physical

properties may result.[29] Pellets containing 40% (w/w) TBW plus high alumina cement (HAC) or Portlant Type II cement were produced by uniaxially pressing slurries at 159 MPa.[62] Half the pellets were cured in air while the other half were immersed in water for two days, then air dried. Density measurements revealed that the manner of curing had no effect on the Type II cement formulation whereas the wet cured HAC samples showed a density increase indicating that the HAC dry cured samples did not contain sufficient water to hydrate cementitious constituents when cured in air. Pellets containing 50 wt % TBW-R, pressed at 172 MPa, and dry cured will be evaluated in static leach and mechanical properties tests.[34]

Basalt-based waste forms have been chosen as an immobilization candidate for evaluation because the TRU blended waste is similar in composition to the natural basalt in the Hanford area. Close equilibrium should exist between a basalt glass or glass ceramic waste form and the groundwaters in a basalt repository. Waste forms were produced by three methods:[62] (1) natural basalt plus 20-30% (w/w) TBW-R was melted at 1350°C, then recrystallized by nucleation at 670° followed by a crystal growth period at 920°C; (2) a second method used 18% (w/w) TBW-R plus chemical oxide additives to give a product with an "exact" basalt composition except for trace amounts of Ni, Cr, and Zn. The mixture was processed as above; (3) 100% TBW-R was melted at 1300°C and then cast into a mold. During recrystallization, the product softened and deformed. Static leach tests and microstructural examinations will be used in choosing a suitable waste form.[62]

Four basalt-based waste formulations were prepared and investigated for the effect of devitrification on the products' chemical durability.[34] The following basalt-like waste forms were produced using the reference blend of nonradioactive sludge and ash from Rockly Flats: (1) TBW-R plus crushed basalt (at 70 and 80 wt % basalt), (2) TBW-R plus chemical additives to make the product composition approximate natural basalt, and (3) essentially 100% TBW-R. All samples were melted at 1300-1400°C, annealed at 550°, and recrystallized by treating for one hour at 670°C and eight hours at 910°C. The samples were leach tested before (glass) and after (glass ceramic) recrystallization. Normalized elemental losses for five elements were determined by emission spectroscopy and are given in Table 2.23 (leaching conditions: static, deionized water, 90°C, 14 d, solution vol./sample SA = 0.1 m).

Reportedly, the improved durabililty of samples BG-20 and BG-30 upon recrystallization indicates that the residual glass phase is fairly leach resistant. It has been reported elsewhere[24] that for a basalt-like waste form, recrystallization resulted in formation of a feldspar phase that improved the waste product's leach resistance by roughly two orders of magnitude. In addition, the sodium leach resistance of the PNL basalt glasses was not greatly improved in any case. This is possibly due to the presence of a Na-rich amorphous glass phase that remains even after recrystallization. Until detailed phase characterization data are available for the PNL basalt-like waste forms for TBW waste blend, the explanation for the improved leach resistance of the recrystallized product appears premature. In fact, due to differences in viscosity at the processing temperature, PNL stated that differences in com-

Table 2.23

Normalized Elemental Losses, g/m^2, for Basalt Based TRU Waste Forms Leached in Deionized Water at 90°C for 14 Days (This is Table 4.1 of Reference 34)

Ion	BG-20[a]	BGC-20[b]	BG-30[c]	BGC-30[d]	SBG-18[e]	SBGC-18[f]	TBWG[g]
Ca	2.85	0.14	3.17	0.29	1.96	0.28	0.62
Mg	2.42	0.26	2.57	0.28	1.76	0.40	0.23
Na	1.95	--	2.74	1.60	1.48	2.96	3.45
Si	2.26	0.21	2.73	0.39	1.69	0.37	1.22
Fe	--	--	--	--	--	0.12	--

[a] Basalt glass with 20 wt % TBW-R, 80 wt % crushed basalt.
[b] Basalt glass ceramic with 20 wt % TBW-R, 80 wt % crushed basalt.
[c] Basalt glass with 30 wt % TBW-R, 70 wt % crushed basalt.
[d] Basalt glass ceramic with 30 wt % TBW-R, 70 wt % crushed basalt.
[e] Synthetic basalt glass with 18 wt % TBW-R, 82 wt % additives.
[f] Synthetic basalt glass ceramic with 18 wt % TBW-R, 82 wt % additives.
[g] TBW-R glass with no additives.

position and yields of crystalline phases are to be expected for the various product formulations.[34] However, regardless of the reasons, it is apparent that the glass ceramic has an improved durability as compared to the glass product. The basalt glass ceramic containing 30 wt % TBW-R was chosen for further leach and mechanical properties testing.

As part of the TRU glass development task of TRUWIP, a study of the tendency of TRU glasses to form spinel devitrification phases has been reported.[34,63] Defense wastes are generally higher in Al, Fe, Ni, Cr, and Mn content than anticipated reprocessing wastes from commercial spent fuel. Similarly, TRU wastes contain more Al, Ni, and Cr. The preponderance of these constituents has resulted in spinel phase formation of the general composition $(Ni, Mn)(Fe,Cr)_2O_4$ in some borosilicate glasses formulated to contain defense or TRU wastes. Although aluminum is not found in spinels, aluminum atoms apparently preferentially occupy sites in the glass structure where Fe, Ni, or Mn are normally located. As aluminum is introduced, these sites are no longer available to the transition metals and spinel precipitation is favored.[63]

For the quantitative determination of the tendency to form a spinel devitrification phase, a series of melts was prepared in which Fe_2O_3 and Al_2O_3 concentrations were varied in a borosilicate base glass composition known to produce spinel crystals. The extent and type of crystallinity were determined by x-ray diffraction. The results in the form of isocrystallinity curves as a function of Al_2O_3 and Fe_2O_3 content are shown in Figure 2.2. Above certain Al_2O_3 and Fe_2O_3 concentrations, increases in either oxide

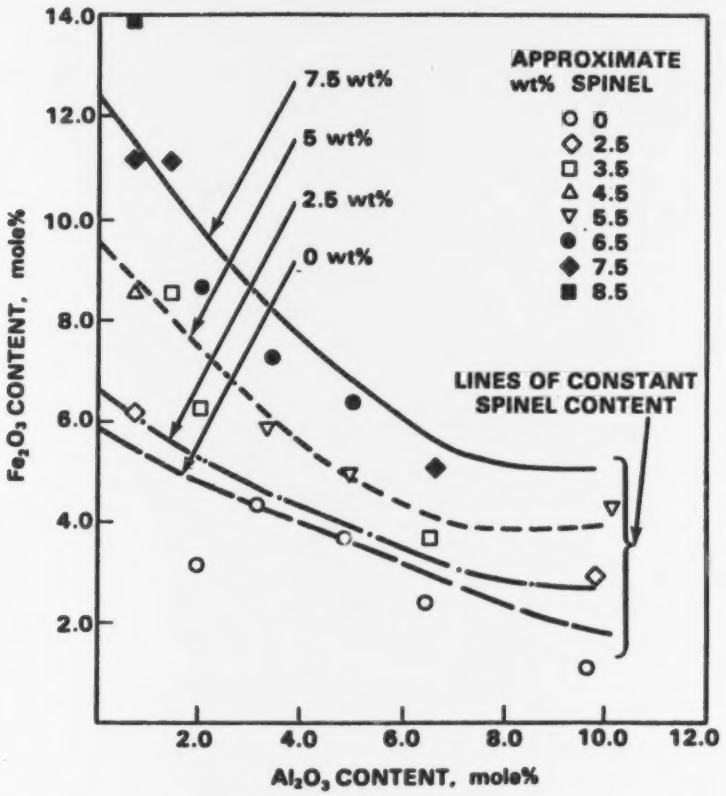

Figure 2.2 Effect of Iron and Aluminum on Formation of Spinel Crystals in a Borosilicate Glass (This is Figure 25 of Reference 63)

enhance spinel formation. Also, at low spinel levels, there is a stronger sensitivity to iron than to aluminum, while at higher spinel levels, the sensitivity to aluminum increases.[63] For the recent PNL glass formulation containing TBW-R, 80-207,[34] the Al_2O_3 and Fe_2O_3 contents do not appear to be high enough to effect spinel phase formation. However, experiments are reportedly planned for glasses containing plutonium-bearing sludge and ash to observe the Pu behavior in the solid matrix as well as during leaching reactions.[34]

PNL has prepared some glass samples which contain plutonium from 30 wt % TBW and a borosilicate glass frit.[62] The ash in TBW was a 50:50 mixture of cold rotary kiln ash and Pu-contaminated ash from RFP. The weight fraction of plutonium in the glass was not reported. Samples were subjected to the MCC-1

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static leach test and the first of these had an apparent normalized Pu loss of 2.8×10^{-5} kg/m^2 (seven days, 90°C, distilled water).[62] This result is only preliminary since the sample surface area was not accurately known.

Low melting temperature borosilicate and high temperature aluminosilicate glass samples have been prepared that contain 50 wt % TBW. Melts of both glasses were prepared using ten waste component variations and subjected to Soxhlet and buffered acid screening leach tests. We assume these leach tests to be similar in conditions to those described elsewhere.[64] Frit and glass compositions and the ranges of glass composition due to TBW variations for the two glass types are given in Tables 2.24 and 2.25 below. Glass samples having the highest alkali content had the highest leach rates. However, since other glass properties met minimum screening criteria for all waste variants, these glass samples were included in the comparative assessment evaluation.

Specimens of glass 80-207 containing 50 wt % Am- and Pu-contaminated TBW-R have been leached up to 28 days using the draft MCC-1 procedure:[65] static deionized water, 90°C, leachant volume to sample surface area of 0.1 m, and time periods from 1 to 28 days. For the pH region of interest, 9.1 to 9.5, the data suggest that a maximum concentration of plutonium ($\sim 10^{-10}$ M) may be limiting the actinide release. Based on earlier work on the leaching of plutonium from glass beads and the predicted solubility of PuO_2(c) at a pH of ~9.5, this limiting concentration may be the solubility limit of PuO_2. Experiments are reportedly planned to measure the PuO_2 solubility limit in higher pH regions.[65]

This completes the discussion of PNL's comparative assessment study of the TRU Waste Immobilization Program. Waste form candidates containing the reference TRU blended waste have been prepared and will be evaluated by a series of standard materials characterization tests during FY 81. Other programs that have been completed at PNL and are pertinent to this review include: (1) a laboratory feasibility study on the formation of silicate ceramics from TRU blended waste and selected additives, (2) glass formulation experiments for incinerator ash, and (3) a generic solubility study for TRU waste oxides in borosilicate glass. These topics will be discussed below.

2.6.4 Sintered Silicate Ceramics

Scoping studies on the feasibility of producing a durable sintered ceramic waste form from TRU wastes and selected additives have concentrated on two simulated waste residues, i.e., RFP blend and RFP alpha ash.[66] The function of the network additives is twofold:[62] (1) to interact with certain species of the waste to form crystalline reaction phases, and (2) to form a matrix surrounding the waste particles. The following mixtures were prepared:[67] (1) neat waste (reference case), (2) waste plus commercial glass frit at 50 and 67 wt %, (3) waste plus silica at 50 and 67 wt %, and (4) waste plus bentonite clay at 50 and 67 wt %. Pellets 1.6-cm diameter by 1.3-cm long were formed by cold pressing at 140 MPa and then sintered for two hours at temperatures ranging from 700°C to 1100°C. A subset of promising samples was selected for charac-

Table 2.24

Chemical Composition of Borosilicate Glass Frit, Glass Containing Reference TBW, and Range of Glass Composition Due to Variation in TBW (This is Table 4.2 of Reference 34)

	Composition, wt %		
Compound	Glass Frit 80-226	Glass 80-207 (50 wt % TBW-R)	Variation in Glass Due to TBW
Al_2O_3	--	3.4	2-5
B_2O_3	18.6	9.5	--
CaO	12.9	10.1	8.12
CuO	4.6	2.3	--
Fe_2O_3	--	10.0	8-12
K_2O	3.7	1.9	--
Li_2O	3.7	1.9	--
MgO	3.0	3.8	2-5
Na_2O	7.4	6.8	5-8
P_2O_5	--	2.5	1-4
SiO_2	39.8	40.5	36-44
TiO_2	2.4	5.0	3-7
ZrO_2	4.6	2.3	--
	100	100	

Table 2.25

Chemical Composition of Aluminosilicate Glass Frit, Glass Containing Reference TBW, and Range of Glass Composition Due to Variation of TBW (This is Table 4.3 of Reference 34)

Compound	Composition, wt % Glass Frit 80-227	Glass 80-208 (50 wt % TBW-R)	Variation in Glass Due to TBW
Al_2O_3	11.9	9.4	8-11
CaO	14.4	11.2	9-12
Fe_2O_3	--	10.0	8-12
K_2O	1.1	1.0	--
MgO	2.8	3.8	2-5
Na_2O	5.8	5.9	5-7
P_2O_5	--	2.5	1-4
SiO_2	54.9	47.9	44-51
TiO_2	5.5	6.3	5-8
ZrO_2	3.6	1.9	--
	100	100	

terization of density distribution of particle size following impact event, leach resistance, volatility, and sintering behavior.[63,68] These data are summarized in Table 2.26.

The leach resistance as a function of additives, additive loading, and sintering temperature was determined for four of the waste elements. Leachate analyses were conducted for Na, Cr, Al, and Si. Results are presented in Figure 2.3. The results of these "accelerated" leach tests indicate an increased leach resistance for pellets containing additives and fired at higher temperatures to produce durable crystalline phases. Pellets containing 67 wt % bentonite and fired above 900°C were judged best. No actinide doping or leach measurements were performed for these sintered ceramics. A plutonium leach rate range has been reported for ceramic waste forms made from, among other things, contaminated incinerator ash plus additives.[69] Leaching experiments reportedly

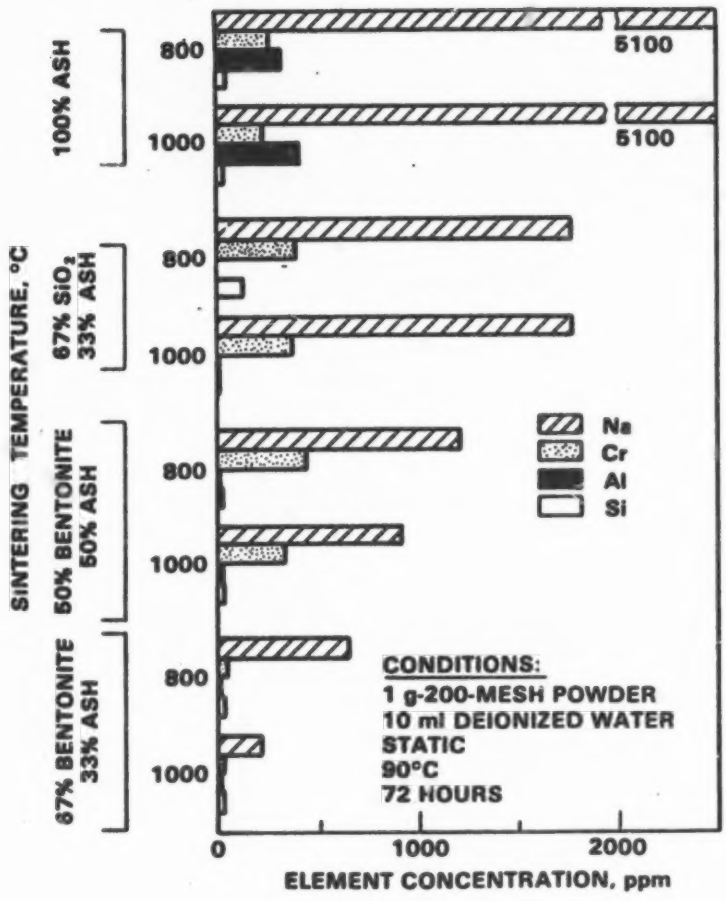

Figure 2.3 Solution analysis of leachate from TRU waste forms containing ash. (This is Figure 1 of Reference 63. For the pellet dimensions given in Reference 63, an elemental concentration of 1000 ppm corresponds to a leach rate of about 3×10^{-4} g/cm^2-d.)

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Table 2.26

Properties of Sintered Ceramics Made From TRU Waste Plus Additives

Composition	Volatility[a] (wt %)	Bulk Density (g/cm^3)	Impact Behavior[b] (wt %)	Porosity (vol %)
TRU blend + additives	6-13	1.32-2.16	7-17	17-54
Alpha ash + additives	1-15	1.11-2.10	3-23	14-60

[a] Weight loss that occurred during sintering.
[b] Expressed as the (respirable) weight fraction produced by impact that is <37 μm.

were performed at room temperature in distilled water and saturated salt brine according to draft ISO procedures. After three months of leaching, the Pu leach rates were in the range of 10^{-8} to 10^{-6} g/cm^2-d. Based on their scoping study, PNL drew the following conclusions:

(1) The properties of typical TRU incinerator ashes and waste blends can be improved by using appropriate additives to form sintered ceramic waste forms. Silica and bentonite were found to be better additives than the commercial silica.

(2) The thermal and physical properties that were measured were rather insensitive to choice of additive. The leachability, however, was not as insensitive and was the most important parameter to consider in the selection of additive.

(3) Samples with 67 wt % bentonite and fired at high temperatures (1000°C) have considerable potential for TRU ash and blended waste immobilization.

2.6.5 Borosilicate Glass Development for TRU Waste Residue Immobilization

Prior to inception of the comparative assessment study, a program to develop borosilicate glasses for immobilization of TRU waste residues was already underway. The main purpose of the effort to be described below was to test the feasibility of adapting high level waste processing technology to large scale production of glass from RFP rotary kiln incinerator ash and to observe large-scale melting properties of the RFP bulk ash glass. However, a more fundamental objective of this particular segment of TRUWIP was development of borosilicate glass formulations capable of accepting a mixture of several TRU solid residues (e.g., chemical process sludges, filter media, and resins) at high waste loading yet remaining relatively insensitive to expected variations

in feed composition. However, as noted elsewhere,[63] the extent to which a glass formulation (or any waste form) is compatible with the waste stream variation will reflect a balance among the waste loading desired, compositional variation that can be incorporated, and chemical durability required. The latter requirement may not be of great concern because of the decision concerning disposal of defense transuranic waste.[70]

Initial scoping studies focused on the incorporation of seven different waste types into eleven different glass compositions.[64] The various waste types were dominated by incinerator ash because of a dearth of compositional data for other solid wastes. Glasses that met criteria for homogeneity, porosity, etc., were further characterized according to leach resistance, viscosity, and electrical resistivity. Because existing HLW vitrification processing was to be used, a large part of the glass formulation effort was devoted to finding a frit composition that met performance and processing parameters. A high alumina concentration is undesirable because of the high melting temperature required. In order to maintain a high waste loading, network modifiers were added to reduce the viscosity caused by the alumina. However, a high alkali content can be detrimental to the glass' leach resistance. A bulk sample of cold rotary kiln incinerator ash received from RFP for the pilot plant scale vitrification process demonstration was found to have a relatively high alumina content.[71] Further glass development for the process deomonstration led to a glass composition (see Table 2.27) that represented the best compromise for desired waste loading, processing requirements, and scoping leach tests. The waste oxide loading of the glass is

Table 2.27

Composition of Glass 79-160

	Weight Percent		
Element	In Frit	In Ash	Glass
SiO_2	25.9	13.8	39.7
B_2O_3	11.9	--	11.9
Na_2O	11.2	--	11.2
Li_2O	2.0	--	2.0
K_2O	4.0	--	4.0
CaO	7.0	--	7.0
TiO_2	4.0	1.3	5.3
ZnO	4.0	0.8	4.8
Al_2O_3	--	11.0	11.0
Fe_2O_3	--	1.1	1.1
BaO	--	0.4	0.4
Other	--	1.6	1.6
	70.0	30.0	100.0

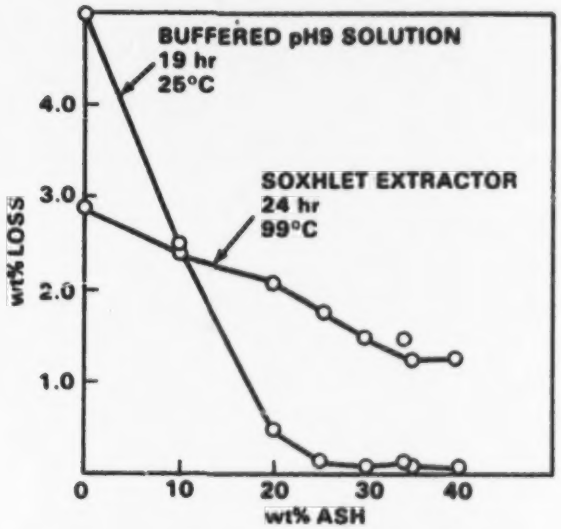

Figure 2.4 Dissolution of Glass 79-160 as a function of weight weight percent ash (This is Figure 11 of Reference 63).

30 wt %. The results for two types of short term scoping leach tests are shown in Figure 2.4. The weight loss is lowered with higher ash content due to SiO_2 and Al_2O_3 from the ash and the dilution of the B_2O_3 and alkali oxides in the frit.[63] Improvements in chemical durability due to increased SiO_2, Al_2O_3, and Fe_2O_3 content has been observed in other glass development work at PNL.[72] The weight loss of 79-160 in a pH 4 scoping leach test was significantly higher than for the pH 9 and Soxhlet tests, probably due to the relatively high boron and alkali content.

Results of the experiment conducted at PNL to evaluate the feasibility of adapting the HLW in-can melting (ICM) process to production of TRU ash glass have been reported.[59,73] A preblended mixture of rotary kiln incinerator ash from RFP (30 % by weight) and frit 79-161[63] were charged into the ICM canister (20-cm dia. by 1.5-m long) and melted at 1030° to 1060°C. Two problems arose during the pilot scale experiment. First, some separation of ash from glass formers occurred. This reportedly did not effect phase separation. Secondly, the reducing environment due to the presence of carbon in the ash depleted the zinc oxide in the glass. The elemental zinc was reoxidized above the glass surface. Also, due to insufficient oxidation, a sintered carbonaceous mass formed at the top of the glass phase. The zinc oxide depletion was found to be less than 5 wt %. The nature and consequence of the carbonaceous material was not discussed. Weight loss measurements for glass samples taken from the monolith were in good agreement with the Soxhlet and pH 4 static tests conducted on the lab-scale melts.[59] No experiments on 79-160 containing actinides have been conducted. Also, no assessment of the usefulness or success of ICM for TRU ash immobilization was provided by PNL. Processing problems associated with the carbon content of the ash and possible changes required have been addressed.[74]

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2.6.6 Generic Solubility Study for TRU Waste Oxides

A study of the solubility of non-radioactive waste components in borosilicate glass was undertaken[63,74] because significant quantities of low solubility components (e.g., Cr_2O_3, Al_2O_3) may limit the waste loading which can be achieved while maintaining adequate chemical durability. In this study, each waste oxide was added individually to the base glass at various levels and its solubility limit was determined. The composition of the base glass and the oxides that were added are listed in Table 2.28, which indicates the solubility limit at 1050°C for the various oxides in this glass. Higher melting temperatures would result in increased solubilities for some components, such as Al_2O_3 and Fe_2O_3. Changes in the glass composition may also be made to increase solubilities. These changes, such as increased B_2O_3 or Na_2O, will tend to decrease the chemical durability of the product. Other observations included:

(1) All components except chromium formed chemically durable crystals in the glass when the solubility limit was exceeded. Chromium formed durable Cr_2O_3, but also a water soluble alkali chromate phase. This phase was found to float on the surface of low viscosity glasses and was dispersed in high viscosity glasses.

Formation of the alkali chromate phase could be controlled through the use of reducing agents. When alumina was present in the glass at less than 4 wt %, the presence of carbon during melting increased the solubility of chromic oxide to 3 wt %, well above levels expected for sludge and ash. When alumina concentrations were excessive, carbon additions did not entirely eliminate the chromate phase. However, sufficient residual carbon will normally be present in the ash to be effective for glasses containing most ash and ash/sludge blends.[74]

Table 2.28

Solubility Limits of Various TRU Waste Oxides in a Representative Borosilicate Glass Melted at 1050°C

Base Glass Composition wt %		Solubility Limits of Oxide Additives wt %(a)	
SiO_2	59.0	TiO_2	10
Na_2O	12.0	Al_2O_3	6
B_2O_3	15.0	Fe_2O_3	10
CaO	4.3	Cr_2O_3	<1
ZnO	7.5	NiO	2
K_2O	2.2	CuO	6
	100.0		

(a) Remainder is reference glass.

(2) Interactions between waste components were also studied. When significant concentrations of alumina (Al_2O_3) were present, the solubility limit of chromic oxide was reduced to about 0.1 wt % and iron solubility was also reduced. The presence of 8 wt % titania (TiO_2) also limited ferric oxide additions to less than 2 wt %. For a blend of sludge and ash, however, the interactions at waste loadings as high as 50 or 60 wt % are not sufficient to cause macroscopic heterogeneity.[74]

PNL plans to handle the problem of waste variation mainly by limiting the waste loading to nominally 40 wt % in their glass formulations.[74] Other approaches include increasing melt temperatures or changing the glass composition.

2.7 Synthetic Monazite

Synthetic monazite has been investigated as an alternative waste form for containment of high level actinide wastes[75,76] and has been suggested for use in the immobilization of TRU-contaminated incinerator ash.[77] McCarthy et al. have suggested that synthetic monazite should be an ideal host for actinides on the basis of the natural mineral's geologic and radiation stability and high solid solution capacity for actinides. At this time, we are not aware of any program underway within DOE that specifically addresses the use of monazite for immobilization of any of the generic TRU waste groups identified elsewhere.[38]

2.7.1 Chemical and Structural Properties of Natural Monazite

Natural monazite is a solid solution mineral based on the larger lanthanide (La Gd) orthophosphates, $LnPO_4$. More specifically, it is a thorium bearing phosphate of the rare earth elements La, Ce, Pr, Nd, Pm, Sm, and Eu. The remaining rare earth elements are occasionally present. Small amounts of Ca, Mg, Fe^{2+}, Al, Zr, Mn, Be, Sn, Ti, Ta, yttrium earths and several percent silica may be present. Uranium is common, but rarely exceeds 0.5 weight percent. Monazites are known with as much as 31 wt % ThO_2[78] and 16 wt % UO_2.[79] Traces of plutonium and neptunium have been reported in monazite and other uranium containing ores.[80] The monazite structure is monoclinic and the natural mineral is reported to have 8-coordinated Ln sites and 4-coordinated P sites.[77] Recent evidence indicates that the lanthanide coordination number may be variable depending on the amount and types of impurity atoms. Beall et al.[81] have found that the structure of single crystals of $CePO_4$ is composed of 9-coordinated Ce atoms. One of the interesting features of the lanthanide orthophosphates is that there is more than one crystalline form.[75] Monazite is the monoclinic (high-temperature) form of lanthanum phosphate or cerium phosphate. If a crystal is grown at a temperature below 400°C, a low temperature hexagonal form will be produced. Above 400°C, the monoclinic form is obtained. The hexagonal form is metastable and once it has transformed from the hexagonal to the monoclinic form it cannot revert to the hexagonal structure. The monoclinic structure is therefore the stable form for the rare earths in the first half of the transition series. A tetragonal form characterizes the rare earths in the second half of the series. In most natural monazites, the actinides U and Th substitute in part for Ln with charge balance

provided by accompanying substitutions of monovalent or divalent cations on the Ln sites and/or Si on the P sites. Huttonite, the high temperature polymorph of $ThSiO_4$, has the monazite structure, so there might be complete solid solution between $LnPO_4$ and $ThSiO_4$. Small percentages of Al_2O_3, Fe_2O_3, and CaO are commonly present. Their solubility in a single phase material such as monazite is important to the formation and stability of the synthetic mineral and, as such, will bear heavily on the choice of this material for immobilization of a waste stream such as TRU contaminated sludge and ash.

2.7.2 Chemical and Physical Properties of Synthetic Monazites

Several studies have been conducted, mainly at ORNL, with an understanding on a microscopic level of the solid state chemical and physical properties of mixed lanthanide-actinide systems as their goal. These properties have been investigated by several spectroscopic methods and the results of the studies are summarized below. The preparation of pellets from monazite powders by a method known as molten-urea coprecipitation will also be discussed. The chemical durability and radiation stability of monazite will be dealt with in separate sections.

Single crystals of every member of the lanthanide transition series (except $PmPO_4$) have been prepared.[75,76,82] The orthophosphates $LaPO_4$ through $GdPO_4$ have the monoclinic monazite structure, while $TbPO_4$ through $LuPO_4$ have the tetragonal zircon structure. These crystals were then used in an array of spectroscopic investigations that included optical, electron paramagnetic resonance, Mössbauer, Raman, and X-ray techniques. Results of these studies are discussed forthwith.

(1) A more accurate determination of the X-ray crystal structure of $CePO_4$ has been carried out.[81] The findings that the structure accommodates such chemically diverse cations as Ca^{2+} and Pb^{2+} in its structure, supposedly due to the irregular coordination around the metal ions reducing symmetry constraints, is certainly encouraging in terms of the constituents of a nuclear waste stream that the crystalline material will have to contain. However, as concerns a TRU waste stream, just how much of the non-actinide material monazite can incorporate is still an open question.

(2) Mössbauer spectroscopy has been used to examine the electronic state of neptunium as an impurity in $LaPO_4$.[76] Crystals of $LaPO_4$ doped with Am-241 were compared to crystals containing Np-237. Americium-241 converts to Np-237 by alpha decay. In the decay process, a recoil Np nucleus can produce significant local disorder and result in a low concentration compound which may be compared with Np as originally grown in a single crystal. The Mössbauer shift results indicate that the charge state of neptunium in the Np-doped orthophosphate is at the lower edge of the nominally 5+ charge state.[76] This is fairly consistent with data from optical absorption measurements (see below) that have shown Np to be tetravalent. Results for the Np charge state due to Am-241 decay are

not as conclusive. Although americium is trivalent in the crystals, after decay, the Mössbauer spectrum shows a pattern consistent with 3+ and 5+ neptunium. However, it has also been suggested that the observed spectrum is due to a single 4+ state that has been split due to electric quadrupole or magnetic hyperfine interactions.[75,76] The implications concerning leachability due to a change in valence from trivalent americium to pentavalent neptunium have been recognized.[82]

(3) The valence states of several actinides in doped crystals of $LaPO_4$ have been determined by optical absorption spectrophotometry. Lanthanum orthoposphate was chosen for these studies because it is transparent in the spectral region of interest. Single crystals of $LaPO_4$ were doped with the following actinides: U-238 (1.7 wt %), Pu-242 (5.0 wt %), Am-241 (0.2 wt %), Cm-246 (0.2 wt %), and Np-237 (2 wt %). The valence states of the actinides were found to be U^{4+}, U^{3+}, Pu^{4+}, Am^{3+},[75,76,82] and Np^{4+}.[83] The valence state of Cm was not conclusively identified.[83]

(4) The use of electron paramagnetic resonance (EPR) spectroscopy has been used extensively by the group at ORNL to investigate the solid state chemical properties of crystalline materials. EPR can be used as an analytical technique for the identification of paramagnetic impurities or defects in solids. The type of information relevant to the understanding of crystalline nuclear waste forms that is provided by EPR can be summarized as follows:[84] (a) the number and position of EPR lines give impurity identification, valence, and site-symmetry, (b) the intensity of the EPR lines is proportional to the number of impurities, and (c) the width of the EPR lines is affected by defects and strains. The investigations at ORNL have dealt largely with examinations of iron group, rare earth, and actinide impurities in both zircon structure and monazite structure orthophosphates.

A large body of data is available for single crystals and powders of rare earth orthophosphates doped with gadolinium. This lanthanide has been shown to exist as Gd^{3+} in the orthophosphates studied.[75] Gadolinium was chosen as a dopant for these studies because Gd^{3+} has an electronic configuration chemically similar to that of the actinide ion Cm^{3+}, its magnetic resonance spectrum is readily observable at room temperature, and its spectrum gives a clear indication of the local symmetry at an impurity site. For the orthophosphates studied, it was found that Gd^{3+} occupies a substitutional rare earth site in zircon[85] and monazite[86] structure single crystals rather than an interstitial or other position. Further, results for hot pressed pellets prepared by molten urea coprecipitation also confirmed that Gd is at the lanthanide substitutional site.[75,85,86] This result is rather significant since it shows that a complicated processing sequence similar to what would be required for large scale waste form production apparently has not resulted in the generation of a nonstoichiometric material whose lanthanide or actinide impurities have become complexed with possible point defects or converted to the

occupation of interstitial positions. Similar behavior has been found for Fe^{3+} in single crystals and powders of $ScPO_4$.[84] As for Gd, an enriched isotope of neodymium, Nd-145, is being used to probe the behavior of trivalent uranium in synthetic monazites.[87]

An interesting observation[75] for some lead containing orthophosphates is that apparently, due to solid state chemical restraints of the host lattice, lead is "forced" into the trivalent state upon incorporation from the lead pyrophosphate flux used in the crystal preparation, where the lead exists in the divalent state. How widespread this behavior is in terms of various lanthanide and actinide impurities and the series of orthophosphates studied at ORNL is not known. Symmetry constraints in rare earth orthophosphates have been discussed elsewhere.[81] Another important point concerning these materials is that the same valence state for a given impurity will not necessarily be observed in different lanthanide orthophospates. For example, trivalent uranium only has been identified by EPR in tetragonal orthophosphates[75] whereas trivalent and quadrivalent uranium has been found in monoclinic orthphosphates.[83] A detailed understanding of factors affecting actinide (and other impurities) charge state behavior in synthetic monazites will require additional investigation.

Because of the relatively large electric field splitting of ground state Gd^{3+}, changes in the linewidths of its EPR spectrum have been used to monitor deviations in the local crystal environment about the ion. EPR linewidths are sensitive to defects and strains in the crystal structure. One such experiment that used the Gd^{3+} "probe" monitored changes in the local impurity environment of single crystals of $LaPO_4$ made from varying amounts of orthophosphate and simulated PW-4b calcine.[84] Conclusions from this experiment were that the PW-4b samples still retained the monazite structure, Gd^{3+} linewidths were broadened due to the simulated waste impurities, and the inhomogeneous line broadening was due to the distribution of impurities in the crystal. The use of the Gd^{3+} probe is being investigated as a means of measuring metamictization phenomena in orthophosphates due to alpha particle and alpha recoil events.[84,87]

Calcined powders of $LaPO_4$ and $CePO_4$ prepared by a urea coprecipitation process were hot and cold pressed into pellets under a range of controlled conditions.[75,88] Factors such as pressure, temperature, duration of sintering, and ratio of urea to lanthanide were investigated for their effect on pellet density. The synthetic monazite powders were made into pellets according to the following procedures:[88] using a cold-pressing technique, calcined $LaPO_4$ powders were mixed with a small amount of binder consisting of steric acid plus acetone. The resultant mixtures were uniaxially compressed, typically for 15 minutes, at various pressures. In most instances, this procedure resulted in the formation of coherent cylindrical pellets. The pellets were then sintered at temperatures ranging from 1000° to 1300°C for time periods that

varied between 8 and 160 hours. In the hot-pressing technique, $LaPO_4$ and $CePO_4$ powders, without any binder, were formed into pellets at 1100°C and 275 bars. Portions of these pellets were then sintered at 1000° or 1300°C, usually for 8 hours. The results of these studies are summarized below:

(1) Urea added in the process is used to control the phosphate particle size, which decreases as more urea is added.

(2) For cold pressed $LaPO_4$ pellets:

   (a) higher pressures resulted in higher densities with the maximum being reached at 34 MPa,
   (b) higher temperatures yielded higher densities but no significant increases were observed above 1100°C,
   (c) no density increase was observed by sintering in excess of 8 hours.

(3) For hot pressed pellets, densities >90% of theoretical were readily achieved at 1100°C. No additional density increase was observed upon subsequent sintering. Pellets that were hot pressed for 1 hour at 28 MPa at temperatures ranging from 100° to 1300°C achieved 95 to 97% theoretical density.[75]

Based on these results and some microstructural studies, it was concluded that hot pressing yields a slightly better product but this fact is offset by the increased processing complexity as compared to cold pressing.

2.7.3 Chemical Durability

The geologic stability of natural monazite is invariably given as one of the compelling reasons for investigating this material as an alternative waste form. However, little information is available on the leachability of synthetic monazites. It has been reported that IAEA leach indices were smaller than those reported for grouts and borosilicate glasses by a factor of 16 for $CePO_4$ in 4 M NaCl at 200°C and 1.7 MPa and a factor of 295 for $La(Am)PO_4$ in distilled water at 200°C and 1.7 MPa.[75,76,82] The glass and grout studies were conducted at ambient temperature and pressure. These data certainly do not allow calculation of a fractional annual release rate for actinides. Data for the dissolution of $NdPO_4$ at 25°C have been reported.[89] At a pH of 1.3, the Nd leach rate was <0.1% in 28 days. At a pH of 10.2, no detectable dissolution was observed after 22 days. Comparison MCC leaching studies of doped monazites and glass are in progress.*

2.7.4 Radiation Stability

Monazite is generally regarded as being stable with respect to radiation damage. This suggestion is based mainly on natural analogue arguments. Because

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*Letter from G. W. Beall, Radian Corporation, to D. R. MacKenzie, BNL, Subject: Synthetic Monazites, dated February 5, 1981.

natural monazites have been found to contain relatively large amounts of urania and thoria but are still in the crystalline state, they apparently have a high resistance to metamictization. Metamict minerals are a special class of amorphous materials which were initially crystalline but, due to some process, have become amorphous. Although the exact mechanism for the apparent loss of crystallinity is not understood, radiation damage caused by alpha particles and recoil nuclei is critical to the process.[90,91] Changes in physical and chemical properties accompany progressive radiation damage. One important property that could be affected by metamictization is the chemical durability. Increased leachability due to radiation damage can result from an increased surface area, microfracturing, or a breakdown of chemical structure of the crystalline waste form. It is generally felt, then, that it is important to examine the long term stabilities of natural materials in order to estimate the effects of radiation damage on the properties of synthetic crystalline phases proposed for use in waste isolation. However, several limitations on the use of natural analogue arguments have been noted. We will not discuss these in any detail since they have been thoroughly treated elsewhere.[90-92] Some of the limitations that have been pointed out include: (1) the effects in natural minerals include not only radiation damage but geologic effects as well. These latter effects are difficult to analyze. (2) Radiation damage effects in natural minerals are often annealed out. (3) Important compositional and structural differences exist between natural minerals and radioactive waste form crystalline phases. (4) The sum total of radiation damage effects in the waste form will be different from that in the natural mineral. (5) The question of effect of dose rate has not been answered. In addition, Ewing et al.[90-92] have noted that the fundamental process of metamictization, factors affecting the rate of metamictization, and structural controls on the process of metamictization are poorly understood. The point is that natural materials will not give all the final answers necessary for waste form assessment. This is evident when one considers that synthetic monazites may be used to isolate up to 1 wt % of plutonium + curium + americium.[91] The effects of high alpha particle fluxes and recoil nuclei on monazite phases are not known. For these reasons, areas of research that are in need of some level of effort have been proposed.[90,91,93] One of the objectives of this research is to gain an understanding of the process of metamictization and to obtain data on the solubility and leachability of synthetic metamict minerals which will hopefully provide information on the suitability of monazite as a TRU waste form. As has been noted elsewhere,[91] before monazite, or any crystalline phase, is accepted as a waste form, it must be verified that anticipated compositions are stable and that the phase is not subject to adverse effects from radiation damage.

2.8 SYNROC

This ceramic waste form candidate was proposed several years ago by A. E. Ringwood of Australia for fixation of HLW,[94] and has been undergoing development in this country, (at ORNL,[95-97] ANL,[97] and Lawrence Livermore National Laboratory (LLNL)[97]) as well as in Australia. The three principal mineral phases present in all SYNROC formulations are hollandite, perovskite, and zirconolite. The hollandite can host Sr, Cs, and several other fission product elements. The zirconolite is considered capable of hosting tetravalent

actinides in particular, and the perovskite trivalent actinides and lanthanides as well as a number of elements such as Fe and Al which would be likely constituents of TRU waste.

Although no DOE site has had a program for applying SYNROC specifically to TRU waste, work performed at ORNL has particular relevance to TRU waste forms because it involved the preparation and testing of specimens of the ceramic containing realistic amounts of Pu, Am, and Cm. Some of this material was used for leach testing and some for determination of the distribution of the transuranic elements among the different mineral phases present.

ORNL employed the sol-gel process to fabricate SYNROC in the form of microspheres up to 1 mm in diameter, which could be pressed and sintered into desired ceramic forms.[95] The sintering and pressing processes are important, not only for achieving a high density product, but also for forming the proper mineral phases. At present, the preferred atmosphere for sintering is Ar-4% H_2. All three of the principal SYNROC phases, zirconolite, hollandite, and perovskite, form in this reducing atmosphere, but in other atmospheres tested, hollandite did not form. This is important for HLW applications, since hollandite is relied on to incorporate Cs and Sr, but might be of little or no consequence for TRU waste. So far, sintered gel microspheres have been prepared of SYNROC B with addition of up to 25% simulated waste[95] and of SYNROC D containing up to 70% simulated SRP waste.[96] Excellent quality of the sintered microspheres has been obtained.

After demonstration of formation of the proper phases, partitioning of the actinides into the various phases was studied. Samples of SYNROC B were prepared containing 10 wt % simulated commercial waste and spiked with Pu-239, Am-241 or Cm-244, or all three.* Information combined from a variety of techniques, including optical microscopy, led to positive identification of phases and an understanding of the microstructure. The three principal techniques employed were X-ray diffraction, electron beam microprobe analysis, and scanning electron microscopy with energy dispersive X-ray analysis. The latter was not capable of yielding information on the location of the transuranics in the different phases, but alpha-autoradiography was completely sastisfactory. By this means, Pu, Am, and Cm were all shown to be incorporated only in the zirconolite and perovskite phases, and not in hollandite. The transuranics had been added in amounts from 0.1 to 0.4% by weight of the total mixture, which is at least as great as, and usually much greater than, the amounts which would ordinarily be encountered in many actual TRU wastes, such as incinerator ash, waste sludges, and secondary waste streams from decontamination processes, after combining with SYNROC constituents.

Leach studies on samples spiked with transuranics have been carried out. Testing was still in an early stage for samples prepared by the sol-gel process at the end of FY 1980, but reasonably definitive studies had been done earlier

*P. Angelini et al., Oak Ridge National Laboratory, "Phase Identification and Partitioning of Transuranium Elements in SYNROC", Paper presented at the 82nd Annual Meeting of the American Ceramic Society, Chicago, April 27-30, 1980.

using SYNROC B samples prepared by melting.[98] Leach rates of the latter samples in deionized water, based on the isotopes Pu-239, Am-241 and Cm-244 averaged between 10^{-8} and 10^{-9} g/cm^2-day. Extreme values from individual leachate analyses ranged between 1.4×10^{-7} and 1.2×10^{-10} g/cm^2-day. This is between one and two orders of magnitude lower than data reported by PNL for simulated HLW glasses containing transuranics.[99] An exact comparison of the two materials would require testing under identical conditions, but conditions were similar enough that the SYNROC samples have to be considered as showing leach behavior at least somewhat better than that of the glass samples.

Fractional release rates of the TRU isotopes from these samples were very low. That for the sample with the highest leach rate was only slightly higher than 10^{-6}/yr, and those for the other samples about an order of magnitude lower. This is all the more impressive because of the small size of the samples (0.01-0.1 cm^3) and their relatively large surface area to volume ratio.

A very short (two-day) test was reported by ORNL for a sample of gel-derived SYNROC B microspheres.[98] The leachate was analyzed by the inductively coupled plasma technique for the major metallic constituents of SYNROC--Ti, Zr, Al, Ca, and Ba. Translated into leach rates, the results obtained were as follows:

Ti, not detected ($<2 \times 10^{-9}$ g/cm^2-d)
Zr and Al, not detected ($<5 \times 10^{-9}$ g/cm^2-d)
Ba, not detected ($<9 \times 10^{-9}$ g/cm^2-d)
Ca, (5×10^{-7} g/cm^2-d).

Bearing in mind that initial leach rates are normally considerably higher than rates averaged over longer times, these data indicate extremely low leach rates of the matrix material--at least three orders of magnitude lower than the PNL leach rates of glass (based on silicon), for all consituents except the Ca which was an order of magnitude lower.

The earlier samples, prepared by melting, showed fractional TRU isotope release rates in deionized water considerably lower than 10^{-5}/yr. Assuming no great difference in leach behavior from deionized water to ground water, these samples can be considered to show reasonable assurance that they could satisfy the 10CFR60 release rate criterion with no help from other engineered barriers. The question still remains whether SYNROC containing various actual TRU waste compositions will behave as well. This would be a relatively simple and straight-forward experimental program to carry out, but even without it there is evidence that compositions of most actual TRU waste oxide mixtures would be compatible with SYNROC formulations.

It has been stated[38] that SYNROC technology "would be applicable to only a small fraction of the TRU waste inventory", since presently stored TRU waste is composed of such widely disparate types of materials, including almost half the inventory as miscellaneous metal scrap. This statement may be correct, but it is also misleading, since it applies as well to glass and other candidate waste form technologies, except possibly specially prepared concretes. Standard

treatments (incineration of combustibles and decontamination of metals) would provide mixtures of oxides to which all these technologies would be applicable. The fact that decontamination and incineration are unlikely to be used for WIPP disposal of present inventories has, of course, no bearing on the suitability of any particular technology for handling the waste streams these treatments would generate.

In the case of SYNROC, the amounts and compositions of high-level waste already incorporated (in simulated form) into various formulations cover a very wide range, as illustrated by the data in Table 2.29. These data refer to ORNL formulations, but similar products have been made at ANL and LLNL.[97] The compositions of typical TRU waste (also presented in the Table), while generally different from those of HLW, can really not be termed more variable, and contain most of the same major constituents, such as Fe, Al, Si, and Ca. Also, up to 70% of the simulated SRP composite waste has been successfully incorporated into SYNROC D. Thus, even if certain TRU waste compositions gave unsatisfactory waste forms at such high loadings, it is reasonable to expect that suitable waste forms could be made at much lower, but still acceptably high, loadings.

The component of processed TRU wastes most likely to cause a problem is SiO_2. It can constitute almost half of some wastes, such as the RFP sludge whose composition was used to calculate the typical 3:1 blend composition given in Table 2.22. ORNL's SYNROC D can contain nearly 10 wt % SiO_2 in the final product, but proportions >10% cause unwanted phases to form and interfere with formation of desired phases. Thus, depending on the effects of other constituents, it appears that SYNROC can accept nearly 10 wt % SiO_2, but this might still be considered insufficient to satisfy economic considerations when dealing with TRU waste streams having very high SiO_2 contents.

2.9 Radiation Effects

2.9.1 Introduction

In TRU waste forms, internal irradiation will result almost entirely from the alpha decay of incorporated TRU elements. The recoiling daughter nucleus ($\sim$100 keV) produced in alpha decay efficiently displaces atoms by elastic collisions. The emitted alpha particle, although it carries far more energy ($\lesssim$5 MeV), displaces most of this energy by ionization or electronic excitation. In addition, helium is produced when alpha particles are stopped in matter. The relative efficiencies for the different fundamental processes are illustrated in Table 2.30[102,103]

Large numbers of stable atomic displacements can affect the fundamental structure of solid phases. Ionization effects may be more subtle. Electronic charge transfer can change the oxidation state of radionuclides in solids and in solution, possibly affecting mobility; the chemistry of leachant solutions may also be affected.[104-106]

Perhaps more importantly, ionization can indirectly produce atomic displacements. In matter incorporating molecular species, ionization may

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Table 2.29

Wt % of the Major Inorganic Constituents of Two ORNL SYNROC Products, with Compositions of Some Typical HLW and TRU Wastes for Comparison

Component	ORNL SYNROC B Containing 10 Wt % Simulated Commercial HLW and 0.1-0.7 Wt % TRU Isotopes[a]	Simulated Commercial HLW used by ORNL with SYNROC B[a]	A Final Product SYNROC D Containing 70 Wt % Simulated SRP Waste[b]	A Representative Simulated SRP Sludge used by ORNL in SYNROC D[c]	Incinerator Ash used by SRL in Combined TRU-HLW Study[d,e]	RFP 3:1 Sludge: Ash Blended TRU Waste[f]
Al_2O_3	9.9	--	20.6	46.4	15	7.4
TiO_2	54.4	--	14.3	--	18	7.7
ZrO_2	10.6	17	3.8	--	--	--
BaO	3.8	--	--	--	1	--
CaO	12.5	--	6.7	3.3	24	8.3
NiO	0.9	4	3.4	2.3	--	--
Nd_2O_3	3.0	30	0.4	--	--	--
CeO_2	2.0	20	0.6	--	--	--
$UO_2(U_3O_8)$	0.8	8	2.5	6.1	--	--
SrO	0.8	8	0.3	--	--	--
Fe_2O_3	1.3	13	27.4	31.6	--	16.8
MnO_2	--	--	7.5	10.3	11	--
SiO_2	--	--	7.8	--	16	42.8
ZnO	--	--	--	--	6	--
MgO	--	--	--	--	6	4.3
Na_2O	--	--	3.8	--	--	5.2

[a] Reference 98.
[b] Reference 100.
[c] Reference 96.
[d] Reference 101.
[e] Also contains 3 wt % elemental C.
[f] Reference 60.

rupture molecular bonds and displace atoms. The resulting molecular fragments, or radiolysis products, may then escape from the material. Gas generation due to alpha-radiolysis of molecular species in TRU waste forms has been discussed in Section 4. This topic will not be treated here. There is also a growing awareness that ionization can produce atomic displacements in some insulating solids which do not contain discrete molecules.[107] This "internal radiolysis" is known to occur in several materials incorporating the silicate tetrahedron, which is a common structural unit in proposed waste forms.[108]

Table 2.30

Radiation Effects in Internal Alpha Decay

Radiation	Effect	Efficiency[a]
Recoil Nucleus	Displacement Collision	~2000 $\frac{\text{Displaced Atoms}}{\text{Decay}}$
Alpha Particle	Displacement Collision	~100 $\frac{\text{Displaced Atoms}}{\text{Decay}}$
	Ionization	10^{18} α/g → 8×10^{10} rad
	Helium Buildup	10^{18} α/g → 100 ppm He

[a]Typical value ranges for glasses and ceramics.[102,103]

Ionization is also considered responsible for the formation of alpha-particle tracks in certain insulating materials.[109] The tendency toward formation of these chemically reactive (and highly soluble) track regions varies greatly from material to material. Unlike internal radiolysis, track formation most probably involves collective effects and produces a highly inhomogeneous distribution of atomic displacements. Recently, it has been proposed that alpha recoil tracks may be formed in nuclear waste solids.[110,111] Once a critical alpha recoil density is reached, serious consequences on chemical durability are said to result. We presently view this claim with some skepticism; for further discussion see the Task 1 Report (Section 6) and the Task 4 Report (Section 4.3) prepared under the present contract. Track formation is not commonly reported in nuclear waste solids; the possibility of track formation is not included in the conclusions leading to Table 2.30. However, in view of the pathological nature of the damage produced, even inferential evidence for track formation deserves careful consideration.[110-112]

2.9.2 Radiation Conditions in TRU Waste Forms

Figure 2.5 compares the alpha-decay dose anticipated for commercial HLW glass, defense HLW glass, and "worst case" TRU waste.[103] The worst case TRU

waste is defined as containing 0.6 weight percent Pu. Typical waste is said to contain Pu concentrations of 10^{-3} to 10^{-4} weight percent.[103] There are cases, however, where a waste form TRU loading of 2×10^{-2} weight percent or more may be reasonably anticipated as a result of concentration in processing (see Section 2.6.2). From Figure 2.5 and Table 2.30, one may obtain the (bulk) radiation conditions shown in Table 2.31. This table will serve as a frame of reference for further considerations.

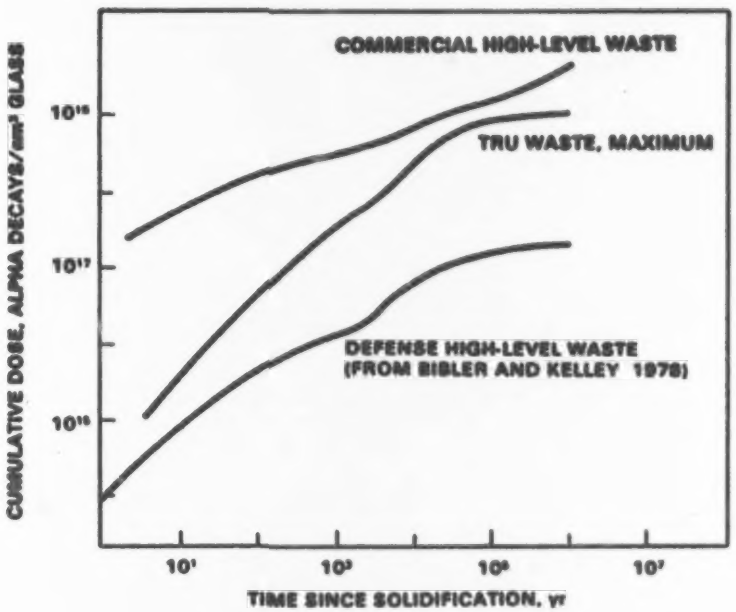

Figure 2.5 Alpha-decay doses for different waste types. From Roberts, et al, reference 103.

2.9.3 Radiation Stability of Candidate TRU Host Phases

There have been few specific evaluations of radiation effects on TRU waste form durability. A number of investigations have been carried out on internal alpha decay effects relevant to isolating the TRU components of high level waste. These are critically reviewed in the Task 1 and Task 4 Reports referred to earlier. The trend has been to infer the durability of TRU waste forms from these studies. Since the anticipated bulk TRU loadings for TRU forms (Table 2.31) are generally lower than those for commercial HLW (Figure 2.5), tests relevant to HLW conditions would seem to provide extreme worst case conditions for TRU waste. We will consider this point further. Here we simply summarize relevant information on the durability of potential radionuclide host phases under internal alpha decay. More detailed information can be found in the Task 1 and Task 4 Reports.

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Table 2.31

Estimated Bulk[a] Radiation Conditions in TRU Waste Forms

Radiation	10^6 Year Dose[b]		Effect[c]	
	Low Loading	High Loading	Low Loading	High Loading
Alpha Recoil	$2\times10^{16}/cm^3$	$3\times10^{17}/cm^3$	$\sim4\times10^{19}$ Displaced Atoms/cm^3 ($\sim7\times10^{-4}$DPA)	$\sim6\times10^{20}$ Displaced Atoms/cm^3 ($\sim1\times10^{-2}$DPA)
Alpha Particle	"	"	2×10^{18} Displaced Atoms/cm^3	3×10^{19} Displaced Atoms/cm^3
			5×10^{8}rad Ionization	8×10^{9}rad Ionization
			0.7 ppm He	10 ppm He

[a]Local conditions will depend critically on the radionuclide distribution

[b]Scaled from figure 2.5 assuming: Low loading = 0.001 wt % Pu; High Loading = 0.02 wt % Pu

[c]Scaled from Table 2.30 assuming waste form density = 3.0 ↔ 6×10^{22} atoms/cm^3. We generally take 10^{19} alpha decays/gram ↔ 1 DPA, neglecting ionization effects

- Concretes

Exclusive of gas generation data, there is little information available on radiation damage in concretes due to internal alpha decay. Weber et al. have reported swelling of less than 0.1 percent for Portland Cement containing 10 weight percent simulated PW-9 calcine, following a dose of 5×10^{17} alpha decays/cm^3.[113] Concretes are complex systems, and the host phases for radionuclides are not well characterized.

- Glasses

Nearly all the relevant data pertain to borosilicate glasses. Depending upon composition, glasses doped with short lived TRU elements may swell or compact as the internal alpha decays build up. Commonly, volume changes

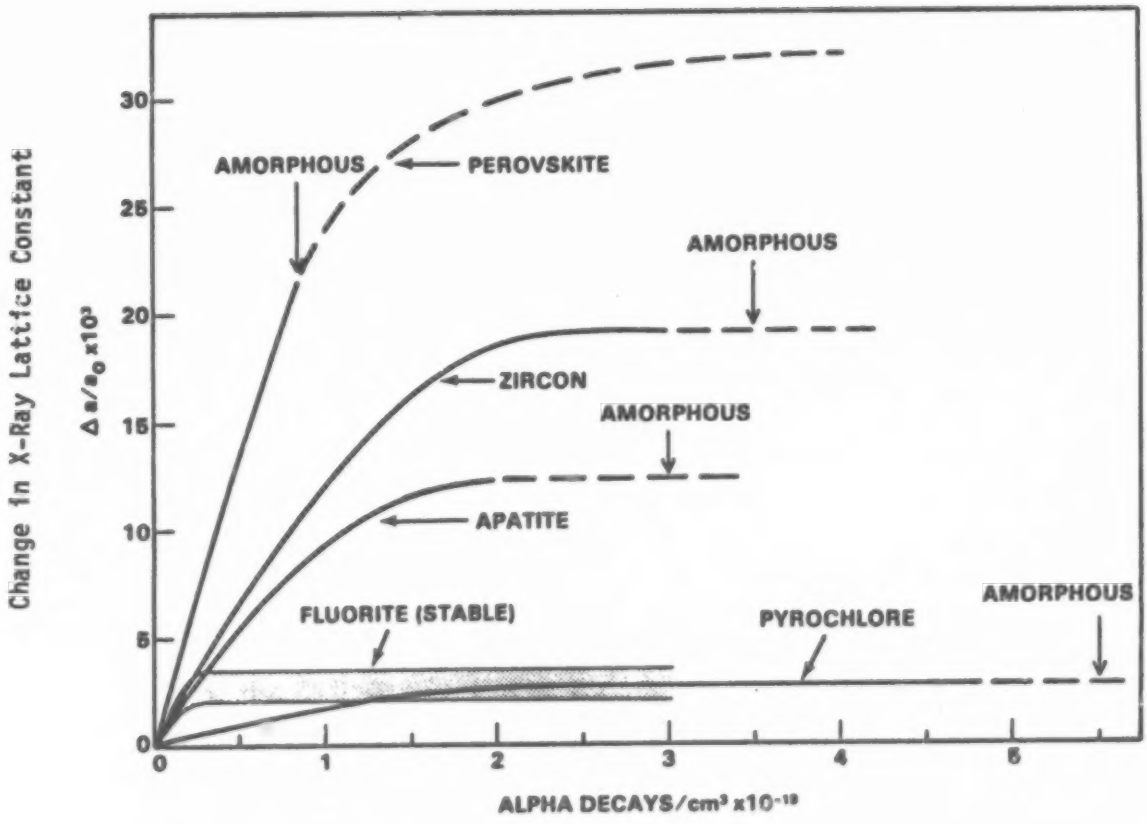

Figure 2.6 Effects of internal alpha decay on various crystal structures. From Weber, Wald and Gray, reference 113.

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saturate exponentially with increasing alpha decay dose: volume changes at saturation are typically 1% or less and saturation is achieved at doses of order 10^{18} alpha decays/cm^3.[103] For internally doped samples there is presently no evidence for radiation induced devitrification or dramatic effects on chemical durabililty. Experiments with external heavy ion bombardment suggest effects on chemical durability following a threshold dose of roughly 2 x 10^{18} alpha decays/cm^3.[110] As mentioned earlier, this suggestion is controversial. Ionizing radiation doses of order 10^{10} rad can cause volume changes in some glasses.[114] Limited experiments on leachant alpha radiolysis indicate no significant effects on waste glass leachability.[115] The chemistry of TRU elements in solution may be affected by alpha decay; this effect is probably not peculiar to a given waste form type.[105,106]

- Ceramic Phases

A large array of ceramic structures occurs as radionuclide host phases or inert phases in crystalline waste forms. These exhibit varying degrees of radiation damage susceptibility. In general, two structural effects may occur under internal alpha decay. First, all ceramics apparently exhibit swelling to some degree; we know of no cases of volume compaction. Second, for sufficient doses, some materials may become X-ray amorphous, or metamict. Very broadly, the ceramic materials may be divided into two classes in terms of their radiation damage responsiveness: stable structures, which exhibit relatively modest swelling (~1%) and remain crystalline to large doses; unstable structures, which swell extensively and are often found in the metamict state. Some examples are given in Figure 2.6. No attempt is made at completeness. Some efforts have been made to rationalize the classification of structures into stable and unstable types.[91,92] Recently, durability of natural analogs for the crystalline phases in nuclear waste forms have been extensively reviewed.[80]

Thus far, there is surprisingly little information by which to directly evaluate the significance of effects such as swelling and metamictization on chemical durability of ceramic waste phases. Intuitively, one expects a greater solubility for the metamict state. However, generalizations are risky. In a notable experiment at PNL, alpha decay effects were studied in a high level waste glass which had been partially devitrified.[116] The curium dopant was found to concentrate in the devitrification phases -- a gadolinium apatite structure and a cubic gadolinium titanate phase. The apatite phase became metamict with increasing alpha decay dose (~1x10^{18} alpha decays/cm^3); this was accompanied by differential swelling, leading to microcracks in the residual glass. Leaching measurements, however, indicated that neither metamictization nor microcracking significantly affected leachability.

The potential importance of rare-earth orthophosphates in the monazite system for TRU fixation has been discussed earlier. For this material, some specific evaluations have been carried out with respect to radiation effects. Evidence derived from natural analogs suggests that monazite forms may be particularly durable.[80,91] Ewing and co-workers have discussed this durability on an empirical basis.[91,92] Materials with the monazite or fluorite

structure are expected to be especially resistant to metamictization (see Figure 2.5). Radiation damage in synthetic monazites has been reported by ORNL. Initial optical measurements on samples doped with 0.5% ^{241}Am showed evidence of color center formation which could be removed by thermal annealing.[82,83] Finally, it is worth noting that monazite systems should be intrinsically more homogeneous than the multi-phase, multi-component systems proposed for HLW forms. Consequently, differential radiation induced stresses would be minimal if the TRU elements are homogeneously distributed.

2.9.4 Discussion and Recommendations

Even in those systems which can be termed unstable in the sense of Section 2.9.3, the available data do not indicate significant radiation effects at alpha decay doses which are substantially greater than those relevant to low loadings in Table 2.31. This is true of ionization effects (other than molecular radiolysis) as well as collision induced displacements. In some cases (alpha radiolysis effects on leachants or actinide solubility, etc.), the data are sparse or inferential. In some situations, it seems that bulk alpha decay doses in TRU waste forms might approach those in current defense HLW -- roughly 2×10^{17} alpha decays/cm^3 in one million years.[103,117] This million-year dose is just about at the detection limit for effects such as swelling, stored energy buildup, etc. produced in laboratory samples. This general trend has fostered the view that existing defense HLW can be converted to crystalline solids or gases without concern for radiation induced changes.[117,118] Analogously, these results have been taken to suggest that radiation damage tests need not be carried out on actual TRU waste forms. (The feeling is, evidently, that in these cases where radiation effects may not be entirely ruled out, the required data will be developed in HLW programs). There is no question that the available evidence points in this direction. However, we feel that certain questions of a confirmatory nature will require consideration; these are discussed below.

- Radionuclide Distribution and Local Radiation Dose

Unlike many of the single phase systems referred to in Section 2.9.3, actual TRU waste forms may be complex, multiphase systems; this is evidently the case for forms prepared by slagging pyrolysis, for example. The local radiation dose due to alpha decay depends on the fine details of the radionuclide distribution over the various phases, which may differ in radiation damage susceptibility. Radionuclides may, perversely, concentrate in phases which are easily damaged. A six-fold concentration of this sort was observed in the PNL work on devitrified glass described earlier.[116] Consequently, some effort should be devoted towards identifying the phases anticipated in actual TRU forms and obtaining realistic bounding estimates of the alpha recoil and alpha decay dose to these phases. Until this is done, generalizations based on bulk loadings must be considered subject to confirmation. For the low TRU loadings, sufficiently conservative estimates appear to be available. Even concentration by factors of 10 or more would still produce relatively low total doses. For the situation in which high bulk loadings (i.e. approaching or exceeding those in defense HLW) may occur, careful characterizations of the TRU distribution should be undertaken.

- Process Latitude

TRU waste streams are inherently more complex than those anticipated for HLW. Accordingly, some information should be collected to ensure that radiation damage susceptibility under repository conditions will not be influenced by variations in the process stream. In supercalcine, for example, McCarthy and co-workers have found that the formation of apatite phases depends sensitively upon the oxidation state of Ce, which is in turn influenced by processing temperatures and uranium content.[119] This phase does not exibit high radiation stability (Figure 2.6). The possibility of increased radiation damage susceptibility due to alteration under the repository environment (say by incongruent dissolution) should also be evaluated.

- General

Some confirmatory consideration should be undertaken to ensure that pathological effects, such as phases susceptible to damage track formation, do not negate the anticipated benefits of low TRU loading. Also, the formation of the metamict state is not well understood, although progress is being made.[90,107] Since the metamict state may not be structurally unique, metamict samples produced in the laboratory may not be exactly equivalent (in terms of durability) to metamict phases in actual waste forms. This is perhaps more properly a concern for HLW forms. Research recommendations are discussed in the Task 1 and Task 4 Reports and in Section 2.7.4 of this report. However, improved understanding of the metamict state, and the metamict "transition" would increase our confidence in the isolation capabilities of TRU waste forms. In particular, additional effort could be directed toward investigating dose rate effects, and establishing the degree of equivalence between the metamict state in natural analogs and laboratory samples. In both cases, the effect of metamicitization on leach behavior should be unambiguously determined.

2.10 Combination of HLW and TRU Waste

Until recently, it was widely accepted that TRU waste would be permitted to be placed in a repository after fairly simple immobilization treatment. For example, in the DOE document "Technology for Commercial Radioactive Waste Management" issued in May 1979, the reference treatment for failed equipment and non-combustible waste was to package it in either 55-gallon drums, 1.2 x 1.8 x 1.8 m steel boxes, or stainless steel containers.[120] The reference treatment included decontamination and disassembly if required. Reference treatment for combustible waste consisted of incineration, followed by immobilization of the incinerator ash in steel drums.[120]

Since HLW treatment involved much more sophisticated and quite different processes than treatment of TRU waste, it was logical at that time to think in terms of separate facilities for the relatively simple TRU waste processes. However, the situation has changed considerably in the last several years so that, as described in this report, processes and waste forms similar to those for HLW have now been developed. Although these more advanced processes will not generally (if at all) be used for the defense TRU waste to be emplaced in

WIPP, some of them may well be required for use with commercial TRU waste which is subject to NRC licensing. That being the case, and since the waste forms we have considered for TRU waste are practically the same as those proposed for HLW (e.g., special cements, glass, ceramics, coated particles), there could be considerable advantage, in economy and convenience, in combining the two types of waste into a single waste form.

2.10.1 Technical Feasibility

Technically, there seems to be no question that such a procedure would be feasible. In terms of radioactive constituents, TRU isotopes would be added to the HLW in amounts comparable to, or only slightly greater than, those already contained in the HLW. With one exception, there are no chemical components of TRU waste streams, whether from incineration and acid digestion or from the decontamination processes we have reviewed, which are not already present in one or another HLW. The exception is elemental carbon found in small amounts in certain incinerator ashes. Since there will be a certain degree of variability anyway in the feed for HLW processing, incorporation of modest proportions of TRU waste should pose little problem with respect to fabrication and properties of a satisfactory waste form. In fact, these should be little different from those of the form produced from HLW alone.

2.10.1.1 Experimental Work with Glass

In the Task 2 Interim Report,[45] we considered the possibility of this combination. At that time, we had seen no references to work on the concept. Since then a PNL progress report[121] was obtained which describes preliminary work in which several borosilicate glass melts were made containing 33 wt % of a simulated AGNS high level waste (PW-7c-1) and 1-3 wt % TRU incinerator ash. The melts were judged on homogeneity, viscosity, and leachability, and the best one chosen (#77-115). No numerical results of the characterizations were given, but it was considered that combining HLW and TRU incinerator ash in a single waste glass appeared feasible. No record of further work could be found and PNL sources were of the opinion that none was done. More recently, a program was undertaken at SRL[101] to investigate the effects on the properties of HLW borosilicate glasses of including TRU incinerator ash and also TRU contaminated electropolishing sludges and HEPA filter media.

Most of the SRL work reported to date has been done with simulated wastes, both HLW and TRU.[101] This was adequate for comparing the properties of glasses with and without TRU wastes, the principal purpose of the study, since the actinide oxides (which were not present) are considered to make up <1% of the SRL TRU waste mixture.

The composition of the simulated TRU ash is given in Table 2.32. It should be noted that it contained 3% carbon. This ash gave uniform melts with standard frits in proportions up to the following:

20 wt % with frit PNL 77-62
25 wt % with frit SRL-21
30 wt % with frit SRL-411

Table 2.32

Simulated Ash Composition
(This is Table 2 of Reference 101)

Component	Wt %
CaO	24
TiO_2	18
SiO_2	16
Al_2O_3	15
Fe_2O_3	11
ZnO	6
MgO	6
BaO	1
C	3

Melts were made with simulated SRP and commercial HLW compositions containing 25 to 33 wt % calcine or sludge, 1 to 10 wt % simulated TRU ash, and the remainder, frit. As an example of the wide variation in HLW compositions used, Table 2.33 gives the wt % values for three different sludge compositions.

Table 2.33

Simulated SRP Sludge Compositions, Wt %
(This is Table 6 of Reference 101)

Component	Composite Sludge	High Al Sludge	High Fe Sludge
Fe_2O_3	31.6	6.0	61.4
Al_2O_3	46.4	86.3	5.6
MnO_2	10.3	4.9	4.1
U_3O_8	6.1	1.5	14.2
CaO	3.3	0.4	4.2
NiO	2.3	0.9	10.5

Satisfactory homogeneous melts were obtained only with the 1 wt % TRU ash mixtures. Whether this could be in any way connected with the carbon content of the TRU ash is not discussed. In any case, this proportion of TRU ash is several times that which would be encountered in practice with both commercial and SRP actual HLW and TRU ash streams.

Leach tests were carried out on crushed samples of all the glasses using a Soxhlet extractor and distilled water. Leach rates, calculated from weight losses, were usually just over 10^{-4} g/cm^2-d, and showed almost no variation

between glasses, with different HLW type and frit, and with and without TRU ash. It was thus concluded that as much as 1 wt % TRU ash can be vitrified with calcined HLW with no adverse effect on glass quality or processing characteristics. Results of one experiment done with 1 wt % actual TRU ash combined with 30 wt % simulated SRP sludge have been reported.[115] Again, the leach rate shows the same similarity to other HLW glasses as was found with the completely simulated series, confirming the conclusion from that work.

SRL also prepared glasses using a simulated composite TRU waste made up of a mixture of 4 wt % simulated TRU ash, 16 wt % HEPA filter media and 80 wt % simulated electropolish sludge. Since vitrification was known to be most difficult to achieve with the high iron sludge (Table 2.33) due to the tendency towards spinel formation, to be conservative, this was the simulated HLW used for the experiments. The results showed that leach resistance was essentially the same as with the other series of glasses. However, only slightly more than half the usual proportion of this HLW could be incorporated into a suitable glass when the glass contained 5 wt% of the composite TRU waste. This means that 75-95% more glass would have to be produced than for the HLW alone.

We have two comments: in the first place, these glasses used a very much higher TRU/HLW ratio than did the glasses made with TRU ash (1:3 instead of 1:25), and in the second place the simulated HLW represented an extreme case. While these conditions constitute restraints required in the SRL study, they are not representative, and we can see no grounds for expecting that this kind of difficulty would be met with the other sludges and calcines used in the TRU ash experiments. Therefore we conclude that, even with waste compositions which are known to be difficult to vitrify, there are no technical reasons preventing formation of satisfactory glasses from HLW-TRU waste mixtures containing reasonable proportions of different types of TRU waste, not merely TRU ash. The presence of small amounts of carbon can apparently even be tolerated.

2.10.1.2 Suitability of Ceramic and Multibarrier Waste Forms

The SRL work does not, of course, demonstrate the concept for waste forms other than glass. Glass properties are considered to be relatively insensitive to composition whereas formation and properties of ceramics and mineral phases are considered to be fairly sensitive. However, this cannot be accepted as a generalization, as exemplified by ORNL's experience with different SYNROC waste formulations in which large amounts of simulated HLW of varying composition have been incorporated into SYNROC waste forms.[96] As pointed out in Section 2.8, indications are that TRU wastes could also be incorporated into SYNROC formulations in reasonably high proportions. Thus, combination of TRU waste with HLW in this waste form in the relatively low proportions encountered in practice ought to be feasible.

Another ceramic waste form which appears suitable for combining TRU and HLW is iron-enriched synthetic basalt (IESB), considered the leading contender for immobilization of TRU waste stored at INEL (Section 2.4). The information so far published on IESB has been concerned with TRU waste only, but enough work has apparently been done at EG&G to show that HLW from various waste streams can

be incorporated into IESB to produce an excellent waste form.* No results have been published so we have not been able to review this work on IESB HLW forms, but assuming EG&G's observations to be accurate, the conclusion must be that TRU waste and HLW would be able to be combined in reasonable proportions in IESB.

Other alternative waste forms such as porous glass and coated particles are insensitive to the oxide composition used, and the coated particles at least should be unaffected by the presence of carbon. Thus, for these latter forms, technical feasibility of combining HLW and TRU waste in the proportions in which they are expected to occur seems assured.

2.10.2 Considerations of Convenience, Cost, and Risk

The argument for combining the two waste streams before processing into a final waste form is largely one of simplification, though volume reduction is also a significant factor. Combination would result in the following simplifications:

- Only one type of waste package (i.e., a HLW package) would have to be handled at the geologic repository.
- A smaller total number of waste packages would have to be handled. This is related to the volume reduction mentioned above. This decrease in volume and number of waste packages might not be large, but could be significant.
- Fewer immobilization facilities would be required. Advantages associated with this smaller number include the savings in plant and equipment, and the decreased handling of the waste with resultant decrease in exposure risk.

Consideration of SRL's experience with their composite TRU waste brings up the following possibility, namely, that the potential decrease in volume and number of waste packages that could be realized by combination would not necessarily be achievable with the same waste form at all immobilization facilities. In other words, not all combinations of wastes will fit a chosen HLW form in the amounts desired. It must also be remembered that there are a number of DOE sites which generate TRU waste but not HLW, and the same situation would presumably exist in the commercial sector once reprocessing is commenced. Thus, in practice, waste would have to be transported from some sites where only one kind is produced, and it must be assumed that TRU waste would always be shipped to an HLW immobilization plant, and not the other way around. The overall result, however, could be a net decrease in transportation, since only part of the TRU waste inventory would be separately shipped; i.e., some would already be at a site having an HLW immobilization facility and would not be shipped anywhere. A possible disadvantage is that whatever amount of TRU waste was shipped would not be in a waste form meeting repository disposal require-

*Letter from D. E. Owen, EG&G Idaho, Inc., to G. Bida, BNL, Subject: Iron-Enriched Basalt Waste Forms, dated May 21, 1981.

ments, thus creating some increase in risk during handling and transportation. This increase in risk would have to be balanced against the decrease achieved by the overall decrease in handling and transportation resulting from fewer total waste packages (of combined waste) from fewer immobilization facilities.

The overall decrease in transportation, the fewer immobilization facilities, the fewer total waste packages to fabricate, and the fewer to transport and handle at a repository, should each result in decreased costs. However, even though the total number of waste packages were fewer, if the number of these combined waste packages were larger than the number of HLW packages which would have been produced in the standard approach, there would be an increase in cost for remote handling which would have to be balanced against the savings due to handling a smaller total number of packages.

The foregoing discussion identifies a number of cost and risk factors involved in an assessment of the possible advantages of combining TRU and HLW, but provides only a qualitative evaluation. It is our opinion that a detailed cost/risk/benefit analysis would have to be carried out before a decision could be made to recommend a general strategy of disposing of all TRU waste by combining it with HLW. However, we feel that such an analysis is unnecessary in certain specific instances, such as generation of both TRU and HLW at the same site, and a high level waste form which accepts TRU waste without an increase in the total volume of products over what would be required for the HLW alone. Under such circumstances, there are definite advantages in using a combined waste form and it would make sense to do so.

2.11 Conclusions and Recommendations

Listed below in abbreviated form are the major conclusions drawn and recommendations made from our review of the literature on transuranic waste form development. Additional discussion of some of the points made below follows this condensed version.

CONCLUSIONS

In addition to being conclusions, some of these points indicate areas that are obviously in need of additional effort if these waste forms are to meet the actinide release rate criterion of 10^{-5}/yr.

- An insufficient data base exists for all the TRU waste forms reviewed.

- In terms of the 10^{-5}/yr actinide release rate criterion, no TRU waste form under development has been shown to meet this requirement with any degree of confidence. In fact, the dearth of available information on the waste forms discussed leads us to conclude, at this time, that no credit can be taken by DOE for the waste form as an engineered barrier.

- In some cases, the TRU waste stream has not been adequately characterized.

- Few data are reported for waste forms containing actual waste.

- Inadequate information exists for the sensitivity of waste form properties to physical and chemical variations in the waste.

- Outside of the comparative assessment study at PNL, no standard test methods have been used in the evaluation of material properties.

- As concerns radiation damage, the available evidence indicates that effects due to alpha particle and recoil nucleus events are not expected to be a determining factor. However, this cannot be confirmed until the ranges of waste form composition and loadings are specified.

- The combination of certain TRU waste streams, e.g. incinerator ash and process sludges, with a HLW stream for processing into a single waste form appears to be a technically feasible strategy based on the available data.

RECOMMENDATIONS

The waste form-specific recommendations are too numerous and lengthy to be listed in this abbreviated section. They appear in the text that follows. Instead, some generic recommendations have been listed below.

- We recommend that the following waste forms be excluded from any further serious consideration as alternative TRU waste forms: (1) the existing TRU waste inventory, (2) Urea-formaldehyde resin, (3) Bitumen, and (4) Normal cast concrete. Reasons for making this recommendation are given below.

- The extent of the solubility of various actinides in glassy and crystalline phases appears to be well known only for borosilicate glass and monazite. This parameter is important because of anticipated variations in the actinide level in some TRU waste streams.

- Data on the phase characterization and actinide partitioning in the candidate waste forms are either scarce, incomplete, or lacking altogether. In the final analysis, these data must be obtained for production prototypic radioactive waste forms. The phases identified for lab-scale samples may not necessarily be representative of those present in large scale products.

- The role of various waste stream constituents in the formation of a durable product should be elucidated. For example, see the discussion on the role that iron plays in IESB (Section 2.4.2.3).

- In the area of radiation stability:

(1) an improved understanding of the metamict state, and the metamict "transition", would increase our confidence in the isolation capabilities of crystalline TRU waste forms. Some effort should be directed toward investigating dose rate effects, and establishing the degree of equivalence between the metamict state in natural analogues

and laboratory samples. Certainly, the effect of metamictization on leach behavior should be unambiguously determined.

(2) The possibility of increased radiation damage susceptibility due to alteration under the repository environment (e.g., by incongruent leaching) should be evaluated.

• There is an obvious need for actinide leach data. In this area, we recommend:

(1) use of standardized (MCC) tests with actual waste loaded samples,

(2) use of waters equilibrated with repository rock and/or potential geologic environments,

(3) that the leach mechanisms for the various waste forms be understood for long term predictive capability,

(4) thorough investigation of the possibility that actinide leach rates are solubility limited at low groundwater flow rates, and

(5) if such is the case, then the concept of valence state control of the actinides in the candidate waste form should be pursued.

2.11.1 Compliance of TRU Waste Forms with Release Rate Criterion

The purpose of this section has been to evaluate DOE efforts in the development of TRU waste forms that comply with proposed NRC regulations,[1] but most notably the adopted actinide release rate criterion of 10^{-5}/yr. We wish to reemphasize here, however, that the release rate criterion is not an NRC requirement imposed on the waste form, but rather a convenient "yardstick" we have adopted by which a meaningful evaluation could be conducted. In this regard, our evaluation is rather limited since it is but one objective that must be considered in the selection of a preferred waste form. Other objectives might include process safety and reliability, waste form flexibility to chemical waste stream variation, and economics. Such considerations are outside the scope of this evaluation; however, we recognize their existence and suggest that such topics receive some attention in any future comprehensive analysis of this nature. Such an analysis for TRU waste forms/processes has been conducted by DOE through the TWSO.[38] This preliminary assessment has addressed such topics as the applicability of the waste forms to immobilization of the TRU waste inventory, and the complexity of conceptualized waste forms production processes.

At the risk of being redundant, the incentive (let alone requirement) for DOE to develop TRU waste forms that meet a 10^{-5} annual release rate criterion, or any release criterion, does not exist any more for two reasons: (1) the present wording of 10 CFR 60 requires DOE to show that the engineered system meets the numerical performance objective of an annual release of radionuclides present in TRU waste no greater than one part in 10^5 of the total

activity present at the time of decommissioning,[1] and (2) the decision to dispose of the existing defense TRU waste in WIPP precludes the need to develop durable waste forms because no actinide release criterion exists for this facility. About the only incentive to develop a relatively durable TRU waste form, at this stage, is the recognition that the waste form is a major barrier in the isolation and containment of radionuclides. The extent to which DOE will pursue further TRU waste form R & D with the objective that the release rate requirement be assumed by the waste form will quite likely be dictated by the extra expense that might be incurred in reducing a waste form's actinide leachability.

In the discussion that follows, we draw conclusions based on our review of DOE programs and make recommendations for consideration in the development of waste forms that will meet the actinide release rate criterion. While the discussion comments on the informational shortcomings of the DOE effort, it must be remembered that DOE has fulfilled its commitment concerning disposal of defense TRU waste. The recommendations that follow will apply to commercial TRU waste generation in the event of fuel reprocessing, and to the additional information which will have to be provided in order to show that a TRU waste form complies with the release rate criterion. At this time, it is not clear what decisions will be made concerning further TRU waste form R & D within DOE or elsewhere, in the event of commercial fuel reprocessing.

2.11.2 Undesirable Waste Forms

Before proceeding with a discussion of the conclusions based on the actinide release behavior of the glass and ceramic waste forms evaluated in this section, those waste forms that we feel should be dismissed from further consideration because of noncompliance with criteria other than, or in addition to, the release rate criterion will be identified.

Clearly in this category of unacceptable waste forms is the existing inventory of TRU contaminated combustible and noncombustible waste. This inventory includes metal scrap, low specific activity metal and glass, combustible organic waste, and contaminated soil.[38] The most compelling reason for excluding the TRU inventory as an acceptable waste form is that no leach rate data exist for this material. In addition, leaching studies on the existing waste would be experimentally difficult and nondeterminate.[3,4] Since few data exist on the chemical form of the transuranics,[122] any statements regarding the possible low solubility of the actinides in this waste are only speculation. Other reasons for excluding most of the metal scrap and all of the combustible organic waste and contaminated soil from a repository have been discussed in Sections 3 and 4, respectively, of this report.

The other waste forms that we feel should be excluded and reasons for this decision include: (1) Urea-formaldehyde resin--because of its water content (which is corrosive), instability toward radiolytic degradation with consequent gas production, potential for microbial degradation, low mechanical strength, and relatively low leach resistance, this waste form cannot meet

proposed NRC repository acceptance criteria. (2) Bitumen--based on stability to thermal, radiolytic, and microbial attack, in addition to a lack of comprehensive and comparative leach data, bitumen is not capable of meeting NRC repository criteria. The susceptibility of bitumen to radiolytic gas generation and subsequent degradation has been viewed as a serious limitation to its use.[38] (3) Normal cast concrete--recent Pu leach data appear rather promising for this waste form. However, because of high water content, radiolytic generation of explosive gas mixtures can result. Also, most cast concretes have moderate to poor impact resistance, an important consideration in transportation safety. Since it is a simple matter to prepare dewatered concretes that have improved properties to normal cast concrete (with the possible exception of leachability), we recommend that any additional R & D on the use of concrete as a TRU waste form should involve the specially prepared concretes discussed in Section 2.5.

2.11.3 General Conclusions and Recommendations

For the remainder of the waste forms discussed in this Section, some generally applicable conclusions can be drawn. In addition to being conclusions, they point out obvious areas that are in need of some additional effort if these waste forms are to meet the release rate criterion. One of the major conclusions of our review is that an insufficient data base exists for these TRU waste forms. Not only are data lacking in the area of actinide leachability, but data on physical, mechanical, thermal, and radiation stability properties are scarce. This lack of information on the basic physical and chemical properties of TRU waste forms is recognized by DOE,[38,58] and is attributed mainly to the delay in recognition of the TRU waste problem in this country and thus of the need to isolate these radionuclides from the biosphere in suitable waste forms. Other conclusions we have drawn from our review can be summarized as follows:

- In terms of the 10^{-5}/yr actinide release rate criterion, no TRU waste form under development has been shown to meet this requirement with any degree of confidence. In fact, the dearth of available information on the waste forms discussed leads us to conclude that, at this time, no credit can be taken by DOE for the waste form as an engineered barrier. We have drawn this conclusion for several reasons: (1) No comparative actinide leach data are available for making valid intercomparisons. In fact, few actinide leach data are available at all. We have not conducted an assessment of the waste forms' performance with respect to the adopted release rate criterion as has been attempted elsewhere.[38] As noted in that report, such a comparison is of limited value since the leaching experiments were not conducted under standard test conditions. Also, the fractional release rates were calculated[38] based on an assumed waste form geometry and from actinide leach data inferred from other (mainly HLW) waste forms not specifically developed for TRU. (2) The requirement that release rates be predictable to thousands of years with a high degree of confidence demands that leaching mechanisms be understood. Such understanding is seriously lacking for most TRU waste forms. (3) Pertinent data are lacking for properties of waste forms compositionally representative of a final design product. Our conclusion regarding the

actinide release rate behavior of candidate waste forms is not meant to imply that they are incapable of meeting or exceeding the part in 10^5/yr criterion. In fact, the low plutonium leach rates for some waste forms, e.g. CPWF concrete[46] and PNL glass 80-207,[65] would indicate that the release rate requirement could be totally assumed by the waste form. We feel that some additional effort in the area of standardized leach testing under simulated repository environmental conditions will prove useful in deciding what waste form(s) meets the criterion.

- As emphasized elsewhere,[38] the TRU waste inventory has not been adequately characterized. This information is necessary in order to assess the potential utility of waste form products or production scale processes.

- Few data are reported for waste forms containing actual waste. The use of specimens in the characterization effort fabricated under realistic conditions with representative levels of radioactivity cannot be overemphasized.[122]

- The sensitivity of waste form properties to physical and chemical variations in the waste are important to an understanding of the waste forms' behavior, yet inadequate information exists in this area. Some effort into gaining an understanding of the effect of waste variation on waste form properties has been underway at PNL.[63] This was one of the key objectives of PNL's TRUWIP program. We feel that a thorough understanding of the behavior of waste forms dictates the need for some continued effort in the determination of the sensitivity of waste form properties to variations in the waste stream. Such an effort should include the use of actual waste and should cover the range of constituent variation determined from chemical analysis.

- Outside of the comparative assessment study at PNL, no standard test methods have been used in the evaluation of properties. At the least, MCC leach testing of the waste forms should be conducted.

- Some waste forms have been suggested for use as encapsulants of size-reduced metal scrap, glass, and other solid trash.[38] These include FUETAP, CPWF concrete, and borosilicate glass. The feasibility of such an approach has yet to be demonstrated.

- As concerns radiation damage, the available evidence indicates that no significant effects due to alpha paricle and recoil nucleus events are anticipated for the actinide waste loadings expected in TRU waste forms. However, because of a lack of knowledge of phases and actinide distribution, and of variations in TRU loading, some experimentation is required to confirm that radiation damage effects are unimportant in certain multiphase crystalline waste forms.

- The combination of certain TRU waste streams, e.g. incinerator ash and process sludges, with a HLW stream for processing into a single waste form appears to be a technically feasible strategy based on the available data.

Consideration of convenience, cost, and risk argues for some additional effort in the development of the appropriate technologies for combining HLW and TRU waste.

In the conclusions listed above, we have given some indication of what types of information are still required for a satisfactory demonstration of compliance of TRU waste forms with a release rate criterion. In what follows, we recommend specific areas where additional effort is required for some of the waste forms in order to understand the behavior of actinide-bearing waste forms in a geologic repository environment. This list is not meant to be exhaustive. Instead, it focusses attention on areas of research that are ongoing within DOE and simply need to be brought to completion and on topics we feel are most relevant to NRC's informational needs.

2.11.4 Waste Form-Specific Recommendations

- Iron-Enriched Synthetic Basalt

Although much information has been generated for this particular waste form, several important questions remain unanswered. We feel that some continued or additional effort is required in the following areas:

(1) Phase and microstrucural data are available for large scale castings of simulated INEL waste and data are forthcoming for lab-scale melts of A-series slag compositions. This latter study is to include the effect of composition and devitrification on the stability and durability of IESB. Since phase formation for IESB is apparently sensitive to several factors (e.g., processing parameters, iron content and oxidation state control, etc.), it is important that additional work in this area identify the phases formed for the "final design" waste product made from actual processed INEL TRU waste. Because this waste form is a multi-phase assemblage, confidence in the long term stability of the actinide-bearing phases will require the determination of phase equilibria so that stability limits, limits of solid solution, competing side reactions, and identity of secondary phases can be specified. The conditions under which host phases are at thermodynamic equilibrium should also be determined. These considerations have been discussed elsewhere.[125]

(2) Seriously lacking are data on the partitioning of actinides into host phases. What actinides partition into what phase (or phases) is an open question. Furthermore, actinide solubility limits for the host phases in IESB must also be determined.

(3) There is an obvious need for determination of actinide leach rates for IESB under standard test conditions. Also, a fundamental understanding of the leaching process is essential. Other issues related to waste form testing and characterization are discussed in greater detail in the Task 4 report prepared under this contract. Such testing should be performed using the final design waste product.

(4) From the information reviewed, it is apparent that the stability and durability of IESB is a strong function of iron content. For example, a high

iron content results in crust formation for large scale IESB castings, and extensive microcracking. However, as discussed in Section 2.4.2.3, the role that iron plays in the chemical durability of IESB is not clearly understood. The leach rates of large scale IESB castings were found to correlate with increasing iron oxide content, which is associated with a corresponding increase in residual glass. The Belgians, on the other hand, have found that the leach rates of silica glasses decreased with increasing concentrations of silicon and four-fold coordinated iron. We feel that some additional effort should be devoted to understanding the effects of composition, including those due to iron and actinides content, on the properties of IESB.

(5) The role that the residual glass phase plays in IESB regarding chemical durability was discussed in Section 2.4.2.3. From that discussion, it is clear that additional work is required in order to determine if, and to what extent, devitrification of IESB affects the chemical durability of these particular basalt glass ceramics. It is generally felt that the durability of glass ceramics can be improved by reducing the residual glass phase content and/or the alkali oxide content in the glass, and there are data that support this claim.[32] However, other data come to the opposite conclusion.[25] Other factors of concern are how the transuranics partition upon crystallization and whether they concentrate in the glass phase or at the crystal-glass phase boundary. Because the factors that govern the chemical stability of glass ceramics in general are not well known, we feel that some effort should be expended in understanding why devitrification improves the leach resistance of some glass ceramics and not others. The focus of this attention should, of course, be on IESB and PNL's basalt glass formulation. Such an investigation should address questions related to the composition of the parent glass and resultant crystalline phases (from devitrification), the behavior of the transuranics (i.e., solubility, partitioning, etc.), the effect of additives on chemical durability and other waste form properties, and the effect of process parameters on product stability. A basic understanding of the type described above could entail a relatively costly long range effort. However, because of the wording in 10 CFR 60 concerning waste forms, there will necessarily be trade-offs in the level of effort pursued in producing a waste form with the lowest release rate reasonably achievable.

(6) Further studies are necessary in order to optimize the electromelt process for production of large scale castings. These informational needs have been recognized and we concur with the recommendations made elsewhere[23] concerning further efforts in this area. This investigation should include the effect of cooling rate on iron oxide content of the glass phase, the extent of microcracking, and devitrification.

- Specially Prepared Concretes

The specially prepared concretes, CPWF and FUETAP, have displayed relatively good mechanical properties, such as compressive strength, and, at least for CPWF, a high TRU waste loading can be achieved. However, there are serious limitations in the data base for these concrete waste forms that need to be considered before any conclusions can be drawn regarding their long term stability.

(1) To date, no information has been published regarding the phase characterization and microstructure of these waste forms. Also, no information exists as to how the actinides are incorporated in these waste forms, what their solubility limits may be, and whether the host phases are thermodynamically stable. Should multiple phases exist, actinide partitioning among them must be determined. The question concerning the nature of the composition of final product concrete waste forms has been raised elsewhere.[38] Since the publication of such information is long overdue and necessary for waste form evaluation purposes, we strongly recommend that additional research on specially prepared concretes should make phase characterization and actinide incorporation high priority topics.

(2) In line with (1) above, phase formation should be investigated as a function of the variability in the waste stream being immobilized. As an example, a typical combustible feed stream from MF reportedly contains 6 wt% metal.[39] Although the resultant ash is sintered at 800°C, some residual metal may remain. How this may affect phase formation, and other waste form properties, is open to question. For both CPWF and FUETAP concrete, then, we recommend that the variation in composition of actual TRU waste streams to be immobilized by these waste forms be determined and the sensitivity of waste form properties to these variations be examined.

(3) Because of the nature of the leach data reviewed in Section 2.5.1.1.2 for CPWF ash-cement formulations, we recommend that additional leach tests be conducted for this waste-concrete formulation. We make this recommendation based on the experimental difficulties reportedly encountered during the leach testing of this waste form. While some additional long term leach data are available,[126] we feel that replication in order to establish some degree of confidence is warranted in this case. Also, leach testing of "production-line" pellets according to the MCC-1 procedure should now be underway at MF.[126] Standardized leach testing should be extended to include sludge-cement and bone char-cement formulations. Additional topics related to chemical durability that need to be addressed include pellet porosity considerations (see Section 2.5.1.4), surface layer formation on sludge-cement pellets leached in brine, elucidation of leaching mechanisms, and the use of actual waste loaded pellets. For FUETAP, no actinide leach data are available for concrete samples containing either simulated or actual TRU waste. This is obviously an area that will need additional work in order to evaluate the usefulness of FUETAP as a TRU waste form. Thus, the recommendations made for CPWF concrete concerning standardized leach testing, understanding leaching mechanisms, etc., apply to FUETAP concrete as well.

Finally, as pointed out in Section 2.9.3, little information exists on the radiation stability of specially prepared concretes due to internal alpha decay. Thus, we recommend that some concerted effort be expended in determining the effects, if any, of radiation damage on the stability of CPWF and FUETAP concrete for the TRU loadings anticipated for these waste forms. The kinds of research that should be pursued in establishing the radiation stability of these ceramic waste forms have been adequately outlined in Sections 2.4.2.4, 2.7.4, and 2.9.4 of this report.

• Monazite

Of all the waste forms discussed in this section, monazite is the best characterized in terms of its solid state chemical behavior, e.g., valence state changes, etc. However, in general, the experiments have been conducted using non-radioactive material. Boatner[123] has noted the importance of using actual radioactive material in the investigation of actinide-containing waste forms because the solid state chemistry of the actinides is not the same as that of their rare earth analogs. Areas where additional work is imperative in order to evaluate the usefulness of monazite as a TRU waste form can be summarized as follows:

(1) There is an obvious need to generate actinide leach data according to standard (e.g., MCC) procedures for samples containing representative levels of radioactivity.

(2) Because of the composition of typical defense TRU waste streams requiring immobilization for WIPP disposal, a large weight fraction of non-actinide containing material would have to be incorporated into the monazite. The TRU waste loadings that monazite can accommodate and still remain a chemically durable single-phase material are not known. An alternate strategy, such as that being pursued at PNL,[65] would be to develop a multiple phase assemblage in which monazite is a constituent. Such an approach could also lead to formation of stable non-actinide containing phases by the use of appropriate additives. Also, the TRU waste streams can contain significant fractions of unoxidized metals and carbon. The effect of these constituents on phase formation and material properties must be investigated.

(3) Information needs related to radiation damage and the process of metamictization and its effect on waste form properties have been amply discussed in Sections 2.7.4 and 2.9.4 of this report along with the Task 1 and Task 4 reports prepared under this contract.

(4) To our knowledge, there is no active program within DOE that is focussed solely on the development of monazite as a TRU waste form. The work of Boatner et al., at Oak Ridge and McCarthy et al., at Penn State University has provided some basic understanding of the solid state chemistry of synthetic monazites and the behavior of the actinides in these materials. We feel that some additional level of effort should be expended in order to provide the basic information described above. This information is necessary in order to make a fair evaluation of monazite as a candidate TRU waste form.

• SYNROC

(1) Based on inferential evidence, TRU waste oxide mixtures are compatible with SYNROC formulations. However, an experimental program is mandatory in order to confirm that SYNROC containing various actual TRU waste compositions will have similarly low actinide leach rates as for the doped SYNROC B formulations.

(2) There is concern that the high silica content of TRU waste can result in the formation of certain undesirable phases, including a residual amorphous glass phase.[38] However, the SYNROC D formulation can contain 10 wt% SiO_2 because of formation of nepheline ($NaAlSiO_4$). Thus, the use of SYNROC as a TRU waste form will have to involve a trade-off between high waste loading and the effect of undesirable phase formation on chemical durability. The possibility of coating SYNROC microspheres with pyrolytic carbon (or some other impervious layer), if economically feasible, could allow for the accommodation of a higher silica content while still maintaining a highly leach resistant waste form. Because of the low leachability of actinides from a SYNROC B formulation and the demonstrated success of microsphere production from the sol-gel process and subsequent coating with material such as PyC, we strongly recommend that some effort be devoted to demonstrating the incorporation of TRU waste into SYNROC, establishing the identity of the phases formed, and determining the extent of solubility of actinide and non-actinide oxides in these phases.

(3) Because SYNROC is a multiphase system, actinides will be distributed in more than one phase. Problems associated with and recommendations concerning the anisotropic distribution of radionuclides in multiphase systems have been discussed in Section 2.9.4.

- TRU Waste Immobilization Program

The kind of information that the TRUWIP program at PNL had originally intended to provide was discussed in detail in Section 2.6.1. How much of the original program will be completed by the end of FY 81 will dictate how much additional R&D may be necessary on the waste forms of interest in order to satisfy NRC informational needs. Certainly, at this time, many of the recommendations made above for some waste forms are applicable to the PNL program, e.g., cold pressed concrete and basalt glass ceramic. Because PNL is aware of the information that is needed in the area of TRU waste form characterization and because of the uncertainty in the extent of completion of the comparative assessment program by the end of FY 81, we will not attempt to provide an exhaustive list of specific recommendations, but rather refer the reader back to the original set of general conclusions and recommendations made at the beginning of this section. One comment we would like to make concerns development of glass waste forms for TRU waste. Some information on the behavior of TRU glass can be obtained from work done with glasses developed for HLW, e.g., 76-68. However, because most waste form properties are composition-dependent,[124] we feel that answers to questions regarding the behavior of TRU glass under repository conditions can only come from experiments involving glass fabricated from prototypical TRU waste streams. As a case in point, we note the problems encountered in TRU borosilicate glass development due to the residual carbon found in incinerator ash.[74] This is not a problem in HLW glass formulations.

A final recommendation concerns demonstration of compliance with the adopted release rate criterion. There is an obvious need for actinide leach data. In this area, we recommend:

(1) use of standardized (MCC) tests with actual waste loaded samples,

(2) use of waters equilibrated with repository rock and/or potential geologic environments,

(3) that the leach mechanisms for the various waste forms be understood for long term predictive capability,

(4) thorough investigation of the possibility that actinide leach rates are solubility limited at low groundwater flow rates, and

(5) if such is the case, then the concept of valence state control of the actinides in the candidate waste form should be pursued.

2.11.5 Additional Considerations Regarding Actinide Containment

While we have not outright endorsed any of the candidate waste forms based on actinide release rate, this is not to say that we feel they are incapable of meeting or exceeding the part in 10^5/yr release rate criterion. For example, the low plutonium leach rates for CPWF concrete and PNL glass 80-207 are encouraging. It should be kept in mind that many of the leach rate experiments have been conducted with samples that contain a much higher actinide loading than will be encountered in actual waste products. With some additional R & D, it is likely that some, if not all, of the candidate TRU waste forms discussed in this section will meet or exceed the release limit. We wish to emphasize one final point concerning this evaluation. The waste form is but one barrier in preventing the migration of radionuclides to the biosphere. In fact, for TRU waste, DOE has emphasized the role of both the host rock and backfill in providing efficient, cost effective redundant barriers to radionuclide migration. In addition, the chemical behavior of actinides in a geologic environment is such that the valence state and, hence, the solubility and sorption behavior can be controlled so as to minimize migration via groundwater through a repository. The objective of the engineered system, i.e., a fractional annual release, could then be met by the additional engineered barriers and would be less sensitive to the choice of waste form.

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3. MANAGEMENT OF TRU-CONTAINING WASTES

3.1 Introduction

The purpose of this subtask is to evaluate alternative technologies for decontamination of selected TRU wastes, such as those generated when processing equipment fails or when whole facilities are decommissioned, and for treatment of the secondary waste streams generated. The topics covered in the Interim Task 2 Report[1] have in most cases been updated to cover material published up to about the end of 1980. A number of new topics such as chemical decontamination of metals and acid digestion of combustible waste have been addressed. Review of all these subjects has been greatly facilitated by discussions with DOE personnel engaged in the work and by their referral of relevant documents. The treatment of secondary waste streams from the decontamination processes was only briefly mentioned in the Interim Report.[1] These secondary waste streams are discussed in the present report and the methods of treating them are reviewed.

Decommissioning, or retiring a nuclear facility from active service, requires that its remaining radioactive material be either contained, or reduced to a low enough level that public health and safety are protected. There is a wide variation in size and type of the facilities to be dealt with, and therefore, in the difficulty and complexity of decommissioning them. However, in general, two principal ways of handling the job are applicable to almost any facility: dismantlement, or some form of on-site storage. Dismantlement will result in removal of all radioactive materials so that the site can be restored to unrestricted use. The radioactive materials must then be disposed of in some acceptable way. Decontamination will usually be a requirement prior to ultimate disposal, and in fact, in order to keep worker exposure low, partial decontamination will often be necessary before dismantlement can even be carried out. Thus it is of great importance to develop effective methods for decontaminating a variety of structures and mechanical equipment, made of different materials, both in situ and after dismantling and sectioning.

The importance of having these methods in hand is emphasized by the magnitude of the decommissioning effort which will be required in the next few years, merely to handle existing backlog and without considering facilities which will become due for decommissioning during that time. A recent DOE planning document for the Surplus Facilities Management Program[2] sets forth a 20-year plan to handle the backlog of 87 facilities at a cost of over $400 million, with the bulk of the effort to come in the next ten years.

Decontamination of failed or outmoded equipment has several attractive features and can be considered a preferred alternative to placing TRU waste in permanent repositories. The advantages include: (1) a large volume reduction with consequent reduction in cost of disposal and avoidance of a large amount of transportation and handling of the TRU wastes, and (2) provision for recovery of transuranics and scarce metals.

The different classes of material to be decontaminated can be divided conveniently into two main types: cladding hulls, and failed or decommissioned equipment. They will be discussed under those headings in the review which follows.

3.2 Management of LWR Cladding Hull Waste

Although this subject is of relatively minor concern at the moment, cladding hulls must be considered as potentially making up a sizable fraction of the nuclear waste inventory. Because of U. S. policy in the recent past, light water reactor (LWR) spent fuel (classed as HLW) has been stored rather than chopped and chemically processed at a commercial fuel reprocessing plant (FRP). However, while the West Valley FRP of Nuclear Fuel Services, Inc., was in operation, some 218 metric tons of LWR fuel was processed,[3] generating a considerable quantity of cladding hulls. The policy of not processing cannot be relied on to continue since it is the result of a political policy decision rather than of a scientific or technological problem. There have been pressures for change from sources other than the nuclear industry, which include the government itself. A Ford Foundation report[4] of September 1979 comments that ultimate recovery of plutonium and uranium from spent fuel (i.e. by chemical processing) must be considered now, since classing spent fuel as a waste form is not likely to be accepted by other countries, or even by the U. S. In March 1980, the Government Accounting Office (GAO) in a report to Congress[5] strongly criticized U. S. safeguards practices and policy. Pointing out the large amount of plutonium which will be produced outside North America in the near term, it urged the U. S. to reconsider its bias against reprocessing and throw its full weight behind the international plutonium management and storage regime proposed by the IAEA. The new administration is known to favor increased reliance on nuclear energy. It has not formulated specific plans, but is known to regard reprocessing as a necessary part of any overall nuclear energy program.

Contamination on the LWR cladding hulls consists of residual irradiated uranium not dissolved during the fuel dissolution stage of fuel reprocessing. One method which has been proposed for dealing with the hulls was simply to compact them before disposal. Extensive fuel reprocessing would lead to large volumes of this type of waste, which is well above the 10 nCi/g TRU limit. If a TRU waste package consisting of mechanically compacted hulls in a suitable container were to be permitted in a repository, a three-fold volume reduction could probably be achieved. A similar volume reduction could be obtained by surface decontaminating, since the secondary waste stream would contain roughly 10% of the hull material. Chemical separation of the TRU isotopes would provide a much greater volume reduction, but at the expense of an extra step in the waste treatment. Volatilization of the hulls as $ZrCl_4$ would combine removal of TRU isotopes and recovery of zirconium in a single step, and the TRU waste volume reduction would be much greater than with mechanical compaction. Both decontamination and volatilization permit the choice of recycling the relatively uncommon zirconium if desired.

Many ways of dissolving zirconium alloys in aqueous media are known and have been used in head-end processes for treating solid fuels and fuel cladding.[6] However, these have not been proposed for management of cladding hulls. Instead two general methods have been under development in the U. S. -- processes based on the volatility of $ZrCl_4$, studied by Argonne National Laboratory (ANL) and Sandia; and a method based on surface treatment of the hulls with a gaseous HF-Ar mixture at 600°C, developed by Pacific Northwest Labortory (PNL). Exploratory studies at ANL[7] aimed at development of a pyrochemical process using molten zinc did not show promise and were abandoned.

3.2.1 Chloride Volatility Processes

Two types of chloride volatility processes have been studied - gas phase and liquid phase. ANL has done extensive experimental work on the former, and a small amount on the latter, using $ZnCl_2$ as the liquid chlorinating agent. Sandia carried out a conceptual study of the use of the double salt $AlCl_3 \cdot NH_4Cl$, based on the known properties of this liquid reagent and its reaction with zirconium metal and irradiated zirconium alloy fuel elements.

3.2.1.1 Liquid Phase Processes

3.2.1.1.1 $ZnCl_2$ Process

Results of experiments with molten $ZnCl_2$ are given in ANL progress reports.[7,8] In all experiments UO_2 was added to the melt as a substitute for PuO_2. At 500°C for five hours with a large excess of $ZnCl_2$, less than half the Zr was converted to $ZrCl_4$; however, with near stoichiometric amounts over 80% conversion was obtained and most of the $ZrCl_4$ distilled out of the reaction zone. Less than 1% of the uranium was found in the $ZrCl_4$. Although these results showed promise for the $ZnCl_2$ process, it would certainly have to be tested with Pu-contaminated Zircaloy, preferably with actual irradiated cladding hulls, before being seriously considered as a candidate for a large scale process.

3.2.1.1.2 Liquid Phase Hydrochlorination

Treatment of zirconium alloy fuel elements with chlorinating agents to volatilize $ZrCl_4$ and thus separate zirconium from the remainder of the fuel constituents is named the Zircex process.[6] The gas phase version is essentially the same as the gaseous HCl treatment of ANL described in the next section. The liquid phase Zircex process using $AlCl_3 \cdot NH_4Cl$ was devised to reduce or eliminate some of the engineering problems associated with the gas phase process, particularly dissipation of heat.[6]

Workers at Sandia have proposed the use of this reagent for the first step in a system for overall management of cladding hulls and HLW (or other radioactive waste).[9,10] Their scheme involves chemical conversion of $ZrCl_4$ formed in the initial step to a zirconate ion exchanger, which would then be used to adsorb the radioactive constituents in the waste stream resulting from processing the fuel from which the cladding had been removed. Zirconate ion exchanger has been shown in hot cell experiments to stabilize successfully high level Purex waste. Although conversion of Zircaloy cladding hulls to zirconate ion exchanger has not been demonstrated, zirconium, Zircaloy-2, and zirconium-uranium alloys have been dissolved in $AlCl_3 \cdot NH_4Cl$, and the $ZrCl_4$ distilled.[6]

$AlCl_3 \cdot NH_4Cl$ has many desirable properties as a dissolution and chlorinating agent. It melts at 304°C and dissolves Zircaloy-2 at a rate greater than the chlorination rate with gaseous HCl at a given temperature.[9] Between 350 and 400°C the reaction is rapid and $ZrCl_4$ distills smoothly. The overall reaction, which can be written

$$Zr + 4AlCl_3 \cdot NH_4Cl \longrightarrow ZrCl_4 + 4AlCl_3 + 4NH_3 + 2H_2$$

is endothermic, so that the process does not suffer from the heat dissipation problems of the exothermic gas phase process.[10]

The salt is very corrosive and little work had been done up until 1961 to find corrosion resistant materials of construction.[6] The conceptual study by Sandia did not mention this as a concern so it is probable that by 1977 suitable materials were available. The Sandia study[9] did, however, identify a potential problem with the use of NH_4Cl, and that is the possibility of side reactions of NH_3 and NH_4Cl with the metal chlorides of the cladding waste to form undesirable compounds which might adversely affect the chlorination and distillation process.

3.2.1.2 Gaseous Chlorination

Preliminary work at ANL[11] showed that chlorination at 400°C with HCl gas would volatilize $ZrCl_4$ from the reaction zone and leave uranium behind. Because of the potential explosion hazard from the product gas mixtures containing hydrogen, it was decided to try gaseous Cl_2 as the chlorinating agent. This was done in a series of experiments[12] in which PuO_2 was also included with the Zircaloy tubing to be treated. Since it was known that chlorination of Pu at temperatures of 550°C and above forms volatile tetrachloride, the temperature in the experiments was held at 400°C. Even so, much greater amounts of Pu were found with the $ZrCl_4$ than when HCl was used. The amount was consistently near the 10 nCi/g level, which means that much of the material would still have to be classed as TRU waste unless the 10 nCi/g limit were relaxed. In fact this could occur. EPA has been using a 100 nCi/g limit as a working definition and will almost certainly set the limit higher than 10 nCi/g if not actually specifying 100 nCi/g*.

Two experiments, one with Cl_2 and one with HCl, were carried out with pieces of actual cladding hull which had been irradiated to 6600 MWD/MTU at Dresden. Their purpose was to find how fission products and neutron activation products in the hull waste behaved during chlorination at 400°C. The temperature was difficult to control in the experiment with Cl_2, with the reaction zone running about 10°C hotter than desired. Occasional hot spots on the Zircaloy surface were also observed. In the experiment with HCl, virtually none of the fission and activation products were volatilized with the $ZrCl_4$, but in that with Cl_2 substantial fractions of many of the radionuclides followed the $ZrCl_4$. This means that use of a strong chlorinating agent such as Cl_2 gas at a temperature sufficiently high to form and volatilize $ZrCl_4$ from cladding hulls will also volatilize appreciable amounts of the associated , -activity. Thus, even if the process could be controlled to keep the $ZrCl_4$ product below the 10 nCi/g limit for TRU waste, it might require disposal as a highly radioactive material since it would be unattractive as salvaged material for reuse in the nuclear industry (the only place it could be used). Use of the mild chlor-

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*D. J. Egan, Jr., "EPA's Environmental Standards for Management and Disposal of High Level Radioactive Waste," Paper D-M3 presented at the Materials Research Society Symposium on the Scientific Basis for Nuclear Waste Management, Boston, November 16-21, 1980.

inating agent HCl, on the other hand, could lead to a salvaged product well below the TRU limit, and also acceptable for reuse from the point of view of β,γ-activity.

Table 3.1 gives a comparison of the salient features of the two gas phase and the two liquid phase chlorination processes.

3.2.2 HF-Argon Treatment

The objective of the PNL program in decontamination and densification of chop-leach cladding residues is described in PNL progress reports as follows: "to develop methods for removal of long half-life transuranics from fuel cladding residues and to consolidate the decontaminated cladding into a dense, chemically unreactive form for storage or burial." Their studies have centered on surface treatment with hot gaseous HF-Ar mixtures to accomplish the first part of the objective, and melt densification producing ingots for achieving a satisfactorily dense, unreactive form.

The latter process concerns our task only insofar as any hull residue reaching that stage would still be classed as TRU waste, in which case it should be ascertained that the second part of the objective above can be met. The induction melting process was tested with a number of heats of Zircaloy-4 using CaF_2 flux under an argon atmosphere.[11] The soundness and hardness of the ingots produced were both excellent, well within ASTM hardness specifications for nuclear grade Zircaloy and within acceptable chemical and corrosion resistance standards for Zircaloy-4.[13] Some later heats produced ingots not quite up to the specifications for nuclear grade Zircaloy,[14] but certainly meeting the requirement of "a dense chemically unreactive form for storage or burial" given in the second part of the objective.

For meeting the decontamination objective, laboratory scale experiments were first carried out to demonstrate a method, then pilot scale equipment was designed, assembled and tested. The laboratory experiments to demonstrate satisfactory descaling with TRU removal resulted in the following process:[15] one-hour treatment of the cladding hulls with a 25% Ar - 75% HF mixture at one atmosphere and 600°C, followed by two half-hour rinses at 95°C with an aqueous solution 0.4 M in ammonium oxalate, 0.16 M in ammonium citrate, 0.1 M in ammonium fluoride and 0.3 M in hydrogen peroxide. This treatment removed all visible surface oxide from both BWR and PWR hulls, and achieved excellent decontamination from TRU elements (99.7% in a typical experiment).

The pilot scale plant, designed to process 2 kg/hr of cladding hulls, after a series of mechanical tests with inactive Zircaloy,[16,17] was tested to verify the chemical processing aspect of operation.[18-22] During this phase, several unexpected problems were encountered. Some of these involved mechanical equipment failure and were fairly easily corrected. A more serious problem whose cause was not determined for some time was an excessive temperature rise in the HF reactor which quickly halted experiments each time it occurred. The cause was finally found to be the highly exothermic reaction of zirconium with hydrogen, the latter formed by the reaction of HF with zirconium metal.[21,22] This reaction occurs only with nearly pure HF, indicating that argon was not

Table 3.1

Comparison of Chloride Volatilization Processes

	Gaseous Reagents		Fused Salt Reagents	
	HCl	Cl_2	$ZnCl_2$ Process	$AlCl_3 \cdot NH_4Cl$ Process
Temperature (°C)	400	400	500	350-400
Temperature control	Good	Difficult to control	Good	Excellent
Type of reagent at room temperature	Corrosive gas	Corrosive gas	Solid	Moisture sensitive solid
Hydrogen in off-gas	Yes	No	No	No
Transfer of fission and activation products (including Pu) with $ZrCl_4$	Trace only	Substantial fraction transferred	Process not tested with actual cladding hulls	
Degree of TRU decontamination	Excellent	Difficult to achieve less than 10 nCi/g in final product		

mixing properly with the HF before contact with the hulls. Further equipment modification was to be carried out in order to solve the problem, but the program was terminated before that could be done.[21]

It is clear that the scientific basis for the process is sound and that problems encountered in scale-up were due to design weaknesses. The importance of testing processes on a production scale before placing reliance on them as steps in an actual full scale waste handling system is well illustrated by PNL's experience in this situation.

3.2.3 Secondary Waste Streams

The secondary waste stream generated in the HF-Ar process comprises the aqueous rinse solutions containing solid Zr and fuel constituent compounds such as actinide fluorides. Although an independent review of the management scheme for cladding hulls recommended that bench scale studies of secondary waste stream treatment processes should be carried out,[15] no mention is made of the subject in subsequent progress reports. Since most of the TRU constituents would be in the insoluble fluorides accompanying the aqueous rinse, it should be a simple matter to convert this waste stream to a small volume compatible with any standard TRU waste form. For example, the insoluble fluorides could be removed by filtration and converted to oxides if required. If significant amounts of transuranics remained in the solution, simply evaporating the solution and heating the residue of ammonium salts to decompose them should leave the transuranics and other constituents as oxides, and in very small amount.

In the volatilization processes, the secondary waste stream consists of the non-volatile residues, which are already solid, but not homogeneous. Since stainless steel and Inconel are not chlorinated significantly at 400°C, massive pieces associated with hull assemblies could remain with the residue and would have to be sorted out for separate disposal if a glass or similar waste form were chosen for the disposal of the residue. Also, many of the chlorides in the residue would be hygroscopic and could cause corrosion problems, so would preferably be converted to oxides regardless of the final method chosen for disposal.

3.2.4 Evaluation of Processes

The main characteristics of the chloride volatilization process and the HF-Ar treatment are compared in Table 3.2. Only the decontamination stage is considered in the table because of the difference in final form of recovered zirconium in the two cases, and because the scope of our evaluation does not extend to the recovered product if it does not require disposal. If such disposal is required, the processes could probably be compared equitably on the basis of ingot production in the HF-Ar process and a final product of ZrO_2 in the volatilization process.

In the decontamination stage, the volatilization processes have the disadvantage that all the metal in the cladding hull has to be converted, and not just a surface layer as in the HF-Ar process. The latter is operated at somewhat higher temperature, but both temperatures are moderate. Both methods re-

Table 3.2

Comparison of Cladding Hull Waste Management Methods

	HF-Ar Decontamination Process	Gas-Phase Chlorination Processes	Liquid-Phase Chlorination Process
Temperature (°C)	600	400	350-400 for $AlCl_3 \cdot NH_4Cl$; 500 for $ZnCl_2$
Temperature control	Good control will require very careful equipment design.	Poor with Cl_2; Good with HCl.	Good
Reagent gas mixture	HF-Ar	HCl/N_2 or Cl_2/N_2.	None
H_2 content of off-gas	Small	None with Cl_2 use; appreciable with HCl.	None with $ZnCl_2$; appreciable with $AlCl_3 \cdot NH_4Cl$
Extent of conversion required	Surface only.	Complete chemical conversion of hulls	
Form and type of secondary waste	Liquid - Aqueous solution of ammonium salts containing small amounts of Zr and fuel constituents	Heterogeneous solid. Ferrous metal chunks + actinide and FP chlorides.	
Stage of development	Proven on lab scale; pilot scale testing never finished.	Proven on lab scale with actual cladding hulls. No plans mentioned for scale-up.	$ZnCl_2$ process tried on lab scale. $AlCl_3 \cdot NH_4Cl$ conceptual process is adaptation of the Zircex process used in fuel reprocessing.

quire handling very corrosive and dangerous chemicals. The volatilization processes appear to be at a disadvantage when secondary waste streams are considered because of the presence of unreacted ferrous alloy pieces. However, in comparing the methods it must be remembered that PNL did not use actual irradiated cladding hulls in its process development and did not consider the effect of pieces of hull assemblies on its decontamination-densification scheme. It appears that there would be little effect on the decontamination step and secondary waste stream, but impure or otherwise unsatisfactory ingots presumably would result unless the melting process were modified.

None of the processes were demonstrated on a large scale, although the $AlCl_3 \cdot NH_4Cl$ liquid phase conceptual process is a direct adaptation of the Zircex process which has been used on the plant scale for the head-end treatment of zirconium alloy fuel.

3.2.5 Foreign Processes

3.2.5.1 Sweden's HIPOW Process

As mentioned in Section 3.2, simple mechanical compaction of cladding hulls was at one time proposed as a management scheme in the U. S. However, this would require very careful handling to avoid ignition of the zirconium metal, and the method seems to be no longer under consideration. The HIPOW process, developed with great technical competence in Sweden, avoids any problems connected with the pyrophoricity of zirconium*.

The acronym HIPOW stands for Hot Isostatic Pressing of Waste. Hot isostatic pressing has been in use industrially for the past decade and was first considered for use with cladding hulls in Sweden in 1976. The process involves placing chopped hulls in a metal container, evacuating and hermetically sealing the container, placing it in a furnace in an argon atmosphere, then heating to 1000°C while applying a high argon pressure isotropically to compress the Zircaloy pieces into a single solid block. Since the melting point of Zircaloy is >1800°C, the HIPOW process permits use of more standard materials and equipment than would be required for a process which depends on melting.

In laboratory scale studies titanium was found to be a good container material whereas iron was not satisfactory. The container finally developed for full scale use was double walled, the inner wall being titanium, the outer stainless steel. The cylinder walls have a corrugated shape, as illustrated in Figure 3.1, to allow for a high degree of axial compression. This is not obtained with the regular cylindrical shape, so that a large amount of powder (titanium or zirconium) has to be added to fill the voids in a standard cylindrical container. No such addition is required for the corrugated containers, and a seven-fold volume reduction of the loose cladding hulls is obtained. The process is equally applicable to stainless steel and Inconel spent fuel assemblies which have been separated from the loose hulls.

*H. T. Larker and R. Tegman, "Treatment of Cladding Hulls by the HIPOW Process," Paper D-H2 presented at the Materials Research Society Symposium on the Scientific Basis for Nuclear Waste Management, Boston, November 16-21, 1980.

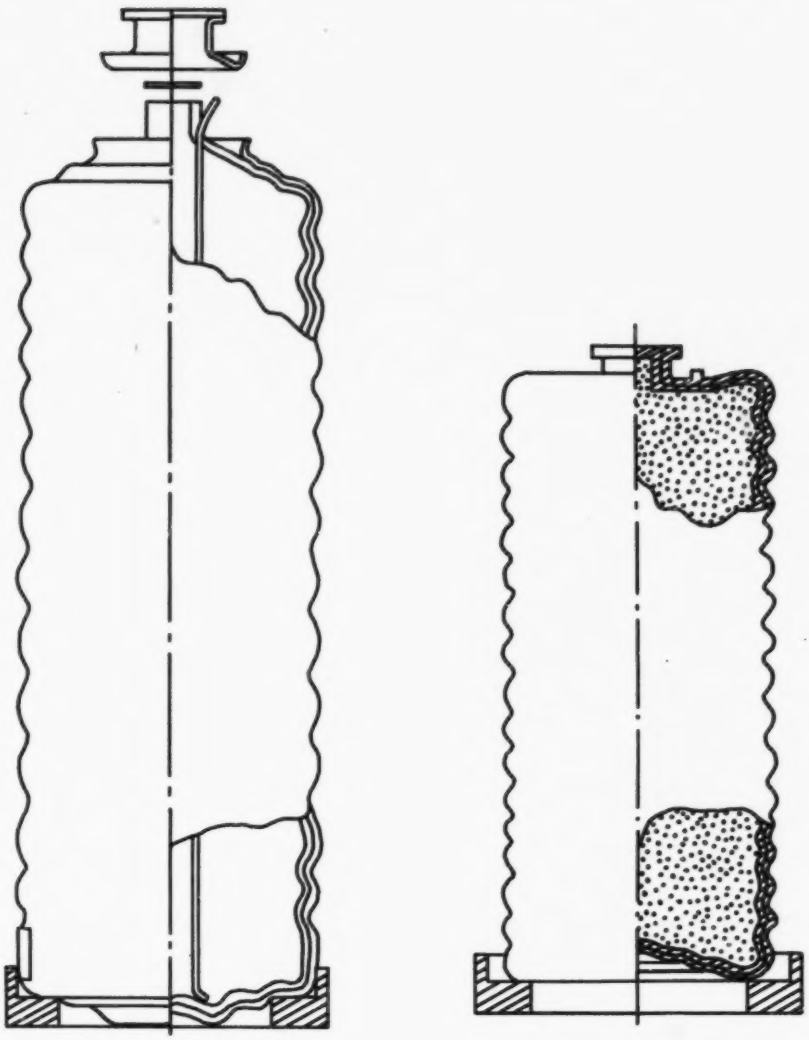

Figure 3.1 Axially resilient, double wall container for the HIPOW process. Prefabricated container with lids and drainage/evacuation tube (left) and filled with Zircaloy hulls and fully densified (right).

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Advantages of the process include:

- Seven-fold volume reduction of the waste stream.
- Very low risk of fire since the high temperature step is carried out with the Zircaloy in a hermetically sealed container.
- Negligible contamination of the high temperature isostatic press, since the hermetically sealed container can be easily decontaminated before going to the press.
- Few and simple processing steps which involve handling of the radioactively hot waste.
- Production of a fire proof and very corrosion resistant waste form.

3.2.5.2 French Process Using Low Melting Zr Alloys

A process being developed by the French CEA is based on the addition of another metal to Zircaloy to form a (relatively) low melting eutectic*. Those of most interest are formed with 17% nickel and 21.5% copper; although 16% iron also forms a suitable eutectic, the authors apparently did not study it. All three melt at around 1150°C. The authors state that mixing stainless steel (316L) hulls with Zircaloy hulls (15-20% by weight) also provides metallic ingots in the same temperature range. This could be a clever way of dealing with cladding hulls where both types are being generated, since it is more difficult to lower the melting temperatures of stainless steels as opposed to Zircaloy. In treating stainless steel and Inconel alloys used in the fuel assemblies, for example, the lowest melting point obtained (with addition of 15% silicon and 4% carbon or 5% boron) was 1250°C, only 200-300° below the original melting point.

The principal advantage of the process is its operation at some 700° below the temperature required for melting Zircaloy directly. It is not known whether extensive segregation of FPs and actinides would occur on cooling the melts. If it did, they would be subject to greater exposure to groundwater in a waste repository than if they were more homogeneously distributed throughout the metal block, as is the case with the product from the HIPOW process. A volume reduction of the loose packed hulls of 5 to 7 is claimed; the former value seems more likely in view of the required addition of the alloying metal, but it is still a reasonable reduction factor. As a waste form the ingots would have to be sealed in a container because of risk of fire when handling. However, it would have good resistance to dissolution by groundwater, and thus provide good protection against release of radionuclides unless segregation was appreciable.

3.2.5.3 Comparison of U. S. and Foreign Processes

The Swedish and French methods for the processing of LWR cladding hulls involve fully densifying the hulls, with no pretreatment, at temperatures far below the melting point of zirconium. This approach is an attempt to achieve a moderate temperature process which ends up with a high quality waste form for geologic disposal. Such an approach has merit where total volume for geologic

*N. Jacquet-Francillon, G. Rabot, C. Sombret and R. Bonniaud, "Melting Process to Condition Decladding Hulls Generated by the Reprocessing of LWR and FBR Spent Fuels," Paper D-J10 presented at the Materials Research Society Symposium on the Scientific Basis for Nuclear Waste Management, Boston, November 16-21, 1980.

disposal is not crucial. In the U. S., where volume is an important consideration and recycling of zirconium may be a desirable option, surface decontamination and chloride volatilization are entirely approproate approaches. This is so particularly when a large TRU waste volume reduction is also achieved, as it would be in the volatilization method, and could also be for surface decontamination with the addition of a chemical step to separate TRU isotopes.

3.3 Decontamination of Facilities and Equipment

Decontamination of equipment, including tools, has at times been undertaken with the aim of reusing them. For this purpose the process used must obviously be restricted to removal of only a very thin surface layer. Methods falling under this heading are chemical, electrolytic and mechanical, and require only ambient or slightly higher temperatures. Failed equipment, and facilities composed of such items as plutonium glove box lines, which are not intended for reuse, can also be handled by these methods, although sectioning beforehand may be required or at least desirable. A completely different type of treatment which can be used when metal equipment is not intended for reuse is the high temperature process of melt-slagging or melt-refining. In all cases the aim is to reduce contamination at least to non-TRU levels so that the decontaminated material can be treated as LLW rather than TRU waste. Some programs had the goal of reducing contamination to background levels so as to be able to release recovered metal for use within the nuclear industry; however, most have been satisfied with achieving LLW status.

3.3.1 Electrolytic Methods

The major recent U. S. effort in developing electrolytic polishing methods has been at PNL. SRP has also been working in this area and has had several small electropolishing units in routine use for some time for cleaning tools and small equipment for reuse.[23] They have designed a relatively large facility (TRU Solid Waste Facility, TSWF) for processing their TRU wastes. Because of the importance attached to volume reduction, a critical part of the TSWF was to be a line of automated electropolishing units. Although this part of the facility has been dropped, the emphasis on volume reduction remains and other means of removing surface contamination will be employed. RFP has worked on developing an electrolytic process based on $NaNO_3$ electrolyte which would avoid the very strong acid electrolyte (usually 85% H_3PO_4) used for electropolishing.[24,25]

The general method of operation in electrolytic decontamination is to remove the contaminant along with a surface layer of metal. This layer is removed by passing an electric current through a suitable electrolyte in a cell in which the piece to be decontaminated is the anode.

3.3.1.1 Pretreatment

An obvious requirement for electrolytic methods is that the surfaces to be cleaned must be conductive. Such coverings as paint, rust, enamel, tape, grease, and epoxy resin prevent current flow and therefore must be removed before electrolytic treatment can be carried out. While a specific chemical such

as a commercial latex stripper will remove certain of the coatings,[19] none is generally applicable. Two methods developed at PNL, liquid honing[19] and vibratory finishing,[17] prepare metal surfaces for electropolishing by easily removing all types of coating. In fact, they do a good job of decontaminating in their own right, as will be described in Section 3.3.3.

3.3.1.2 Tank Applications

This is the standard method for treating relatively large pieces which can be readily attached to racks for immersion in the electrolyte bath. Most development has been put into the electropolishing process. With the equipment in use at PNL,[15] decontamination has been consistently achieved to well below the 10nCi/g limit with electrolysis times of only a few minutes at temperatures slightly above room temperature and using 85% H_3PO_4 as the electrolyte.[15,16] Use of an aqueous $NaNO_3$ electrolyte results in some roughening of the metal surface as the surface layer is removed, as opposed to the smoothing obtained with electropolishing. The former process, termed electrodecontamination by RFP, is obviously applicable to tank use and to the other types of operation to which electropolishing is applied. The characteristics of the process are discussed in Section 3.3.1.5 on alternative electrolytes.

3.3.1.3 In Situ Applications

PNL has recently put considerable effort into development of in situ electropolishing devices using the standard 85% H_3PO_4 electrolyte. Both fixed and movable versions have been used, and are particularly appropriate for handling large pieces of equipment, or facilities such as large plutonium glove boxes.

An early development at PNL was a fixed contact device for use in decontaminating large flat areas such as walls and floors of plutonium glove boxes.[13,18] Flat areas were necessary to permit gasketing of the electrolyte container to the work surface. A typical decontamination factor obtained was 5.5×10^3, which reduced the Pu contamination to below the TRU level.[18] (The decontamination factor is defined as the ratio of activity in the original material to that in the final product.) The method was later extended to use on uniform curved surfaces.[26]

More recent developments include decontaminating interiors of pipes with axially located cathodes, both fixed and movable, and use of movable cathodes of the swab and pumped stream types to decontaminate curved irregular surfaces, corners, grooves, etc.[27] The interior of a 5000-gallon liquid radioactive waste tank was successfully decontaminated using three electrolyte-supplied swabs and two pumped-stream devices;[21] 85% of the internal surface was cleaned with a large swab device with a magnetic coupler capable of remote operation. The cathode area was 60 in^2 and 2 ft^2/min was decontaminated at a current density of 4 A/in^2.

In connection with a study of ways to decontaminate highly oxidized Savannah River HLW canisters,[26] considerable effort was put into development of four different in situ electropolishing devices for accommodating the varied

geometries encountered on the canisters. These devices and their areas of application are described in Table 3.3.

Table 3.3

In Situ Electropolishing Devices Evaluated for Decontamination of HLW Canisters

Type	Cleaning Area, in^2	Use
Pumped stream	1.8	Spot decontamination.
Pumped stream	0.13	Decontaminate inside corners and grooves.
Swab	3.1	Decontaminate curved or ridged areas.
Contact	16.0	Decontaminate flat or uniform curved surfaces; electrolyte is contained within device.

3.3.1.4 Barrel Electropolishing

In order to avoid racking of small pieces, PNL has developed a method for polishing them in a slowly rotating barrel anode.[20] Although the same H_3PO_4 electrolyte can be used for the latter application as is used for the others, current tends to be excessive (200 to 300 A). By using a mixture of H_3PO_4 and H_2SO_4 much lower current is drawn. The rotating barrel was also successfully applied to the removal of uranium contamination from molybdenum pieces. As with the other electropolishing techniques, decontamination to levels well below the 10 nCi/g limit for TRU wastes was achieved.

3.3.1.5 Alternative Electrolytes

For electropolishing ferrous alloys, H_3PO_4 is the electrolyte of choice because it has good throwing power* and can be used at reasonable current densities. For specific applications changes may have to be made, such as addition of H_2SO_4 for the barrel electropolishing. Also, other metals may require alteration of the electrolyte. For example, a mixture of H_3PO_4 and HCl was required for treating B-Cr-Ni alloys.[13]

With any electrolyte the anode surface is dissolved, but polishing or smoothing of the surface at the same time occurs only within a rather narrow range of current-voltage conditions, and with specific electrolytes such as the strong acids discussed in the previous paragraph. With basic electrolytes,

*Throwing power refers to the ability to polish areas shielded from the cathode, such as bolt holes, crevices and surfaces with unusual geometries.

again under the proper current-voltage conditions, relatively uniform removal of the anode surface occurs but the surface becomes rougher. The metals dissolved from the anode surface form hydroxides, or hydrous oxides, and precipitate out of solution. A basic electrolyte developed at RFP contains 200 g/L $NaNO_3$, 20 g/L $Na_2B_4O_7 \cdot 10\ H_2O$ and 2 g/L $Na_2C_2O_4$ or 2.5 g/L NaF.[24,25] An important reason for its development was to reduce personnel exposure in decontamination operations involving high activity levels. Since the removed contaminants precipitated out in the sludge and could be readily removed from the electrolyte, exposures from handling the electrolyte could be greatly reduced.

PNL evaluated the electrolyte and agreed with RFP's assessment regarding ease of removal of contaminants.[20] However, they cite the following disadvantages:

1. Exhibits poor throwing power.
2. Requires high current densities.
3. Operates at relatively high temperature (70-90°C).

While the basic electrolyte has been applied successfully to immersion or tank use, its poor throwing power would make it less suitable for use in the rotating barrel anode device. However, it should be applicable to in situ applications. Its principal attraction remains the great ease of handling of the secondary waste stream.

3.3.2 High Temperature Processes

3.3.2.1 Fused Salt Decontamination

Early work at PNL showed that contaminated stainless steel could be effectively decontaminated using oxidizing fused salts.[28] Decontamination factors of 10^6 or better were obtained using fused $NaNO_3$ at 800°C and several stages of salt-metal contact. The process generated a large amount of contaminated salt, however: a three to one salt-to-metal weight ratio (and even greater volume ratio) was required to achieve a decontamination factor of 10^6. The method therefore could not be considered as a large scale process unless the TRU content of the salt phase could be removed regularly in a small volume (e.g. as oxide precipitate) allowing recycle of the salt.

3.3.2.2 Melt-Slagging

3.3.2.2.1 Development at ANL

Melt-slagging (melt-refining) of steels contaminated with plutonium has been suggested as a possible decontamination process which has the potential advantage of producing steel for reuse and at the same time simplifying analytical problems encountered in keeping track of the plutonium. Such a method was investigated in some exploratory work at PNL in 1973,[28] but partition of the radioactivity between molten stainless steel and a fused inorganic slag was found to favor the metal phase, so the process was not investigated further.

Some years later ANL began a program to test the use of various silicate slags for removal of plutonium from contaminated metal. A number of promising experiments were described in two 1977 progress reports[11,12] and a topical report was published last year[29] which covers the work described in the progress reports and, apparently, all the work done on the project. Sufficient experimental detail is given to evaluate the scientific aspects of the work as well as its usefulness as the basis for a full scale decontamination process. Results from some typical experiments are compiled in Table 3.4. A comprehensive conceptual design for a full scale process is given in the topical report.[29]

In connection with the latter aspect, the relatively high temperature (1500°C) and long heating times (1-2 hours) used are of particular concern. In one experiment the melt was held at 1500°C for only one minute, however, with similar results to the other experiments, indicating that times considerably shorter than an hour might well be feasible.

In terms of the scientific results, the method of setting up the experiments is of prime importance. In most of the experiments contaminated metal samples were simulated by placing PuO_2 in a hole drilled in a piece of stainless steel or nickel and inserting a stainless steel or nickel plug in order to restrict accessibility of the slag to the PuO_2 until the metal had melted. To conduct an experiment, pieces of slag were placed around the metal sample in a recrystallized alumina crucible, the crucible contents melted and held at 1500°C for one to two hours, then cooled so that the phases could be sampled. The interior of the molten metal and fused slag phases were not sampled to determine the concentration of plutonium, so these experiments could not yield true distribution coefficients. The distribution coefficient, K_d, is defined as

$$K_d = \frac{\text{Pu concentration in slag}}{\text{Pu concentration in metal}}$$

A few experiments were carried out in which conditions approached those required for obtaining distribution coefficients. These involved (a) use of a metal sample from a previous experiment, in which the unextracted plutonium was at least partially distributed throughout the (solid) metal, and (b) contacting clean metal with contaminated slag to see how much plutonium partitioned to the metal phase. Too few of the latter two types of experiment were done to permit assessment of reproducibility.

Although true K_d values were not obtained, apparent values are of interest in comparing performance of different metals and slags. The apparent K_d values ranged from 2×10^6 to 8×10^6 for steel, being about a factor of two lower for diopsidic than for borosilicate slag. For nickel with borosilicate slag, apparent K_d was around 5×10^4. Presence of small amounts of copper and brass (up to 5%) had little effect.

This indicates a higher solubility of PuO_2 in nickel than in steels, and such a conclusion is supported by the distribution of plutonium in the different metal samples after slag contacting. Refined analytical methods, including

Table 3.4

Plutonium and Americium Concentrations in Melt Refined Steel
From Some Typical ANL Experiments
Analytical Results for Disk From Middle of Ingot

Experimental Conditions

Initial contaminant concentration, 400-450 ppm Pu and 2.5-2.8 ppm Am
Temperature, 1500°C
One hour contact time
Ratio of slag to metal, approximately 0.1 by weight

Experiment No.	Slag	Contaminant Concentration, ppm		Apparent Decontamination Factor	
		Pu	Am	Pu	Am
76	$CaSiO_3$	0.26	1.6×10^{-3}	1.6×10^{3}	1.6×10^{3}
80	Borosilicate glass	0.22	2.0×10^{-3}	1.9×10^{3}	1.3×10^{3}
101	$CaMgSi_2O_6$	0.18	1.8×10^{-4}	2.3×10^{3}	1.4×10^{4}
107	CaAl silicate	0.10	2.6×10^{-4}	4.2×10^{3}	1.0×10^{4}
109	Borosilicate glass	0.0012	ND[b] ($<10^{-6}$)	3.5×10^{5}	$>2.5\times10^{6}$
113	Borosilicate glass	0.0011	ND	3.8×10^{5}	$>2.5\times10^{6}$
115	Borosilicate glass	0.03	ND	1.4×10^{4}	$>2.5\times10^{6}$
130-2[a]	Borosilicate glass	7×10^{-5}	ND	6×10^{6}	$>2.5\times10^{6}$

[a]Surface of ingot mechanically removed prior to sectioning and analysis.
[b]ND = nondetectable.

autoradiographic techniques and fission track counting of neutron irradiated samples, enabled the authors to map out thoroughly the relative distribution of the plutonium in different parts of the slag and the metals, e.g. near the phase boundary, near the crucible wall, or in the interior of the slag; and on the surface, invisible defects, or throughout the interior of the metal. We judge this information to be of considerable scientific value in contributing to chemical and metallurgical knowledge of the systems studied, even though it does not enable distribution coefficients to be determined.

From the process point of view, it is unimportant whether or not the plutonium in these experiments was ever in the liquid metal phase. Only the extent of decontamination and ability to reproduce it are important. Decontamination factors from the data given appear to be of the order of 10^5 in a number of experiments with borosilicate slag (Experiments 109-115 in Table 3.4), which should be adequate for a viable process. In fact, since most of the plutonium associated with the metals after contacting was on the surface and in visible defects and very little was in the interior, (see, for example, Experiment 130-2 in Table 3.4) it may have been held in tiny pieces of slag adhering to or trapped in the surface of the metal, and actual decontamination therefore might be made even greater if a better way could be found to separate the slag from the metal.

The report suggests that, in a large scale process, a second extraction would be useful. Experiments were, in fact, done which showed that further decontamination was obtained in a second extraction. Even the first extraction was able to reduce the Pu concentration to below the 10 nCi/g limit in nickel as well as steel.

3.3.2.2.2 ORNL Program

ORNL's program to develop a method based on melting for treatment of metal scrap from uranium enrichment plants is described in a 1978 topical report[30] and a conference paper presented this past year.[31] The ORNL effort was able to draw on studies made for the Oak Ridge Operations Office by the National Lead Company,[32,33] as well as those of ANL described in the previous section.

The initial emphasis in the Oak Ridge program was to clean the bulk of metals to the point that they could be recycled either within DOE or as commercial scrap. The contaminants were to be concentrated in a relatively small volume of slag for reclamation or permanent disposal, while metals not decontaminated sufficiently for recycle were to be cast as easily handled ingots for burial or storage in a considerably reduced volume. The emphasis later shifted to the technical and economic feasibility of melting for volume reduction alone. Recently the importance of the decontamination aspect has again been emphasized, with the report titles giving as much prominence to "decontamination" as to "volume reduction,"[34] or even omitting the words "volume reduction."[33] In fact, the program which resulted in the last two reports "was sponsored by the National TRU-Waste Management Program" and contains work with plutonium contamination similar to that done earlier by ANL (Section 3.2.2.2.1). The ORNL study (continuing into FY 1981) covers more metals than did the ANL study, and carried the melt refining process to an

engineering scale demonstration on mild steel, stainless steel, copper and aluminum.

In the conceptual plan,[30] pretreatment consisted of steam treatment followed by sorting to remove nonmetals such as insulation, cement, rubber and plastics. Sorting according to metal would be required only if recovery and recycling of relatively pure metals was desired. If the different metals mixed in a given batch contained aluminum or other low melting metals, the batch would be treated in a moving hearth furnace with different temperatures in different zones. As the temperature increased, paint and scraps of plastic would burn off, then the various metals and alloys would melt and be drained off as their melting temperatures were reached. The high melting stainless steel and superalloys would be collected into crucible charges for an induction melting furnace where they would be melted in a crucible with an appropriate slag and cast into ingots. The lower melting alloys would also be contacted with slag, after being collected in their respective crucibles, and then poured into molds.

Laboratory experiments[31] were carried out to confirm the feasibility of the processes proposed in the conceptual study,[30] and to determine the proper slags and crucible materials for use with different metals.[35] The bulk of this work was done using uranium as the contaminant, but work with plutonium contaminant has been reported[34] for experiments in which various ferrous and non-ferrous metals were contaminated with PuO_2 and melted with and without slags.

Results for experiments with plutonium were comparable to those with uranium, showing a relatively high degree of partitioning into the oxide phase. Table 3.5 shows the distribution between the bulk metal and the surface dross for samples melted without slag.

Table 3.5

Distribution of Plutonium in the Bulk Metal and Surface Dross of Plutonium Contaminated Samples Melted Without Slags

Metal	Plutonium in Bulk Metal (ppm)	Plutonium in Surface Dross (ppm)	Plutonium (Surface)/ Plutonium (Bulk)
Iron	0.25	533	2.1×10^3
Copper	1	15,960	16.0×10^3
Nickel	89	116	1.3
Stainless Steel	121	6,163	50.0
Aluminum	1856[a]	18,287	9.9

[a]This high value probably indicates that a dross inclusion was contained in the metal sample.

Although the plutonium partitioning in general was into the dross, the latter apparently was not easily separated from the metals, so that a slag is necessary for any practical process. Partitioning results obtained for several slags with mild steel and stainless steel at 1600°C were given , and are reproduced in Table 3.6.

Table 3.6

Results of Melt Refining Tests on Mild Steel and Stainless Steel

Sample	Plutonium Content, ppm		Slag	
	Metal	Slag	(Wt %)	Type
Mild Steel Tests				
1	1	1470	10	Borosilicate
2	1	910	10	Blast Furnace
3	2.5	2360	10	High Silica
4	0.6	2280	5	Borosilicate
5	8.6	2670	5	Blast Furnace
6	0.4	3970	5	High Silica
7	8.3	942	10	Basalt
Stainless Steel Tests				
1	1.9	1120	10	Borosilicate
2	0.8	1700	10	Blast Furnace
3	0.5	2240	10	High Silica
4	1.5	3680	5	Borosilicate
5	0.4	2640	5	High Silica

Since the starting material had a plutonium content of 500 ppm, decontamination factors of approximately 300 to 4000 were obtained with silicate slags. This degree of decontamination is quite good, but not as great as obtained by ANL (decontamination factors around 10^5). This may be due to ORNL's higher operating temperature of 1600°C instead of 1500°C creating more problems with crucible materials and thus adversely affecting partition into the slag.

The engineering scale work reported to date[31,34] used uranium as the contaminant and carried out tests to demonstrate that the melt refining process would be feasible on a reasonably large scale. In the demonstration, uncontaminated scrap metal was sorted into copper, stainless steel, aluminum, and mixed metals. The various batches were contaminated by painting with a UO_2-alcohol slurry and then melted under slag, or drip melted in the case of aluminum. The partitioning of uranium into the slag was consistent with results obtained in the laboratory scale experiments. The weight of scrap in the four batches was 218 kg, which occupied a volume of 1.60 m^3. After cutting to fit into the melter, total volume was 0.4 m^3, and after melting and pouring, the volume of the ingots was 0.049 m^3 and that of the slag 0.003 m^3. Total volume reduction thus was a factor of 30, and obviously proves the point of achieving excel-

lent volume reduction with scrap taken from a wide assortment of sources. Certain types of scrap would, of course, show less volume reduction.

The same comments apply to the ORNL laboratory scale experiments as to the ANL experiments. In both studies actual actinide contaminated waste or scrap metal was not used, and the actinide contaminant was simply mixed, as oxide, with the metal. In both studies accurate K_D values could not be determined under these conditions, and similar steps were taken to alleviate the problem. However, in terms of a practical process, as pointed out in the last section (3.3.2.2.1), the degree of uptake of the contaminant by the slag and hence the degree of decontamination is what is important. In view of this, the ORNL process is suitable for uranium decontamination on an engineering scale, and since plutonium decontamination comparable to that of uranium was obtained in laboratory experiments, an engineering scale process for plutonium and other actinides can be expected to be feasible also.

3.3.3 General Methods

It was pointed out in Section 3.3.1.1 that two pretreatment procedures developed at PNL can be considered as decontamination methods in their own right. These two, liquid honing and vibratory finishing, can often decontaminate material to below the TRU limit, and have the added feature that they are applicable to materials other than metal, such as rubber and plastics. Of the two, vibratory finishing is by far the more important, so much so that it is now the standard method for decontamination of failed and discarded equipment at PNL.

3.3.3.1 Liquid Honing

Liquid honing is used in the metal finishing industry to clean surfaces, remove burrs and machine marks, and relieve stress concentrations. It uses a jet of liquid containing abrasive particles directed at the work from hand held guns by a stream of high pressure air. The guns can be designed for specific applications, such as cleaning holes with a large depth-to-diameter ratio. About 0.1 mm thickness of metal is removed during a typical decontamination cycle.

PNL's evaluation of the method[19] showed that in three to five minutes it not only cleaned exterior metal surfaces, but also decontaminated threaded areas and deep into bolt holes, as well as giving fair decontamination factors for rubber surfaces. However, blast from the jet tended to disperse the removed contamination, so that a high degree of operator care with a well designed system would be required to keep loose contamination under control. For areas of appreciable size, the method is tedious and time consuming, so that its principal application appeared to be as an adjunct to a more versatile method.

3.3.3.2 Vibratory Finishing

Metal pieces for decontamination are often corroded or coated with paint, oil, epoxy resins, or other non-conductive material which has to be removed before electropolishing can be carried out. Chemical pretreatment using a commercial latex stripper at 150°F was developed at PNL[21] and successfully

removed organics such as paint, tape and grease, but not epoxy. The treatment often removed most of the alpha contamination as well, but is not applicable to all kinds of surface coverings. Vibratory finishing, on the other hand, was shown to have general application as a pretreatment, and was usually capable on its own of decontaminating not only metal, but also rubber and plastics, to below the 10 nCi/g level.[21] After vibratory finishing, electropolishing could be quickly and easily carried out to reduce alpha contamination to a barely detectable level, several orders of magnitude below 10 nCi/g.

Early work with the process used ceramic cutting media, but this contributed relatively large amounts of both ceramic and metal particles to the secondary waste stream. Now metal media are used almost exclusively, particularly case-hardened carbon steel and stainless steel ball cones, which have the substantial advantage of producing no secondary waste due to media wear.[36] Both types of media produce surfaces which show essentially no radioactivity on smears and which are ideal for subsequent handling and additional decontamination by electropolishing if desired.

The secondary waste produced by vibratory finishing with metal media consists only of the material removed from the surfaces of the contaminated items, such as rust and other corrosion products, paint, scale, dirt and radioactive contamination. This amount is quite small and is flushed away by circulating liquid compound, commonly 10% NaOH solution containing surfactant. Most of the solid waste is removed by filters in the circulatory system, and the liquid compound can be recirculated for a large number of batches before processing is required. This involves evaporating to concentrate to a sludge. The filtered solids and evaporator sludge could be dried and fired to get rid of organic material and form oxides, but in practice at PNL the waste is simply incorporated as is in drums of hydraulic cement.

The vibratory finishing method was originally tested using a 4 ft^3 commercial tub type model, but the presently used annular model has a 12 ft^3 capacity. With its use vibratory finishing has become the standard decontamination method at PNL. Because vibratory finishing of noncontaminated metals and nonmetals is a well established industrial process, it is possible to transfer much of the needed technology, either directly or with minor modifications, to the decontamination application. PNL has discussed the decontamination aspects with a number of companies who either use vibratory finishing for large components, or use automated high volume systems to surface finish smaller items.[36] They conclude that the use of automated vibratory finishing systems to process large volumes of surface contaminated waste, both metallic and nonmetallic, while minimizing personnel exposure and processing costs, is well within the range of existing technology.[36]

3.3.4 Chemical Decontamination

Removal of radioactive decontamination from solid surfaces by treating with various chemical solutions has been standard practice at U. S. and foreign nuclear installations for many years.[37] While much of this effort is applied to decommissioning operations and to treatment of low level waste, certain chemical methods have been designed for TRU contaminated materials and

equipment. Such methods have the virtue of simplicity, since application of the cleaning solutions and collection of the contaminants do not require highly specialized equipment. Specific methods in use or under investigation at Savannah River Laboratory (SRL) and Hanford Engineering Development Laboratory (HEDL) are discussed below. In addition, the Idaho Chemical Processing Plant (ICPP) carries out routine in-cell decontamination of its nuclear fuel reprocessing equipment with chemicals that could be applied to TRU contaminated material, although the ICPP contamination problems are mostly connected with fission and activation products. A comprehensive decontamination manual was issued by ICPP in 1979.[38]

3.3.4.1 Cleaning Pu Glove Boxes at SRL

Work was carried out at SRL to develop a simple chemical method for decontaminating stored bulky equipment, such as Pu glove boxes and cell liners, to below the 10 nCi/g level so that they could be classified as non-TRU waste and removed from retrievable storage.[39] The ultimate goal was said to be complete decontamination, which "may be achievable by electropolishing."

In their testing program, the two highly alpha-contaminated glove boxes which were cleaned had been used for 12 years for handling multigram quantities of Pu-239, Am-243 and Cm-244. Data were collected on the number of man hours required for various phases of the operation as well as on the degree of decontamination achieved and amounts of the chemical solutions used. The boxes were prepared for the tests by removing all loose paint, dirt and other debris by vacuuming the whole inner surface (after scraping off loose paint), then wet wiping the interior surfaces with detergent solution. The chemical technique consisted of washing with alkaline permanganate (3 wt % $KMnO_4$, 16-18 wt % NaOH) and oxalic acid (15 wt %) solutions, with intervening water flushes.

Results for the cleanup of one of the boxes are summarized in Table 3.7.

Table 3.7

Decontamination of Box A

Decontamination Cycle	Volume of Solution, gal	Man-Hours	Activity Remaining mCi	nCi/g
Initial			1620	2050
Wipe down			1300	
1	122	2.5	10.2	12
2	80	2.0	5.0	6
3	40[a]	0.6	4.2	5
4	100	2.0	1.7	2.1
5	90	2.0	1.1	1.4

[a]MP-7, a decontamination agent supplied by Western Reserve Laboratory, Cleveland, Ohio.

After two cycles of alkaline permanganate and oxalic acid washes, the contamination had been reduced below the TRU limit. The first cycle gave a decontamination factor $>10^2$ and each succeeding cycle gave a further decontamination factor of only a factor of two. In treating the second glove box, the first cycle reduced the contamination to below 10 nCi/g, from an initial level more than double that of the first box, yielding a decontamination factor $\geq 10^3$.

It can be concluded that this relatively simple procedure, which requires very few man hours and modest volumes of chemical wash solution, is effective in reducing gross alpha-contamination to non-TRU levels in one or two cycles.

3.3.4.2 HEDL Chemical Decontamination Work

A study was started at HEDL in FY 1979 to develop a redox-nitric acid system for decontamination of failed metal equipment.[40] The progress report just cited[40] covers the period from January to June 1979, and was published in October 1980, so that results from the study after mid-1979 were not available to us.

The system chosen for investigation was the Ce(IV)-HNO_3 system. This reagent dissolves a surface layer from the metal pieces, unlike many of the other chemical decontaminating agents used, such as those discussed in the previous Section (3.3.4.1), but in a manner similar to the dissolution occurring during electrolytic decontamination. Although HEDL's process used electrolysis to keep oxidizing Ce(III) to Ce(IV) as the latter was chemically reduced, this part of the process was independent of the decontamination occurring since the metal being chemically treated was not an electrode. Rates of dissolution of stainless steel were insignificant without Ce(IV) and at room temperature, even in 7M HNO_3. At 90°C even HNO_3 as dilute as 1M was effective in removing a suitable surface layer when the cerium concentration was 0.1M and the ratio of Ce(IV) to total Ce was maintained at a value >0.8. The dissolution rate was affected only slightly by the HNO_3 concentration, but the metal surface was considerably roughened by the higher concentrations. Pu decontamination was ineffective unless Ce(IV) was present, and very effective in the presence of Ce(IV). This is strikingly illustrated by the data plotted in Figure 3.2, for decontamination of two similar stainless steel pieces.

Several potential advantages for this process over other currently used chemical and electrolytic decontamination methods were suggested by HEDL.

- HNO_3 solutions are widely used throughout the nuclear industry and their properties are well known and understood. This should facilitate regeneration of the decontamination solution and recovery of actinides or disposal of TRU waste.

- Use of the HNO_3-Ce(IV) system removes a surface layer which normally ensures thorough decontamination, whereas other chemical agents can be expected only to remove gross contamination (which may, of course, be all that is desired).

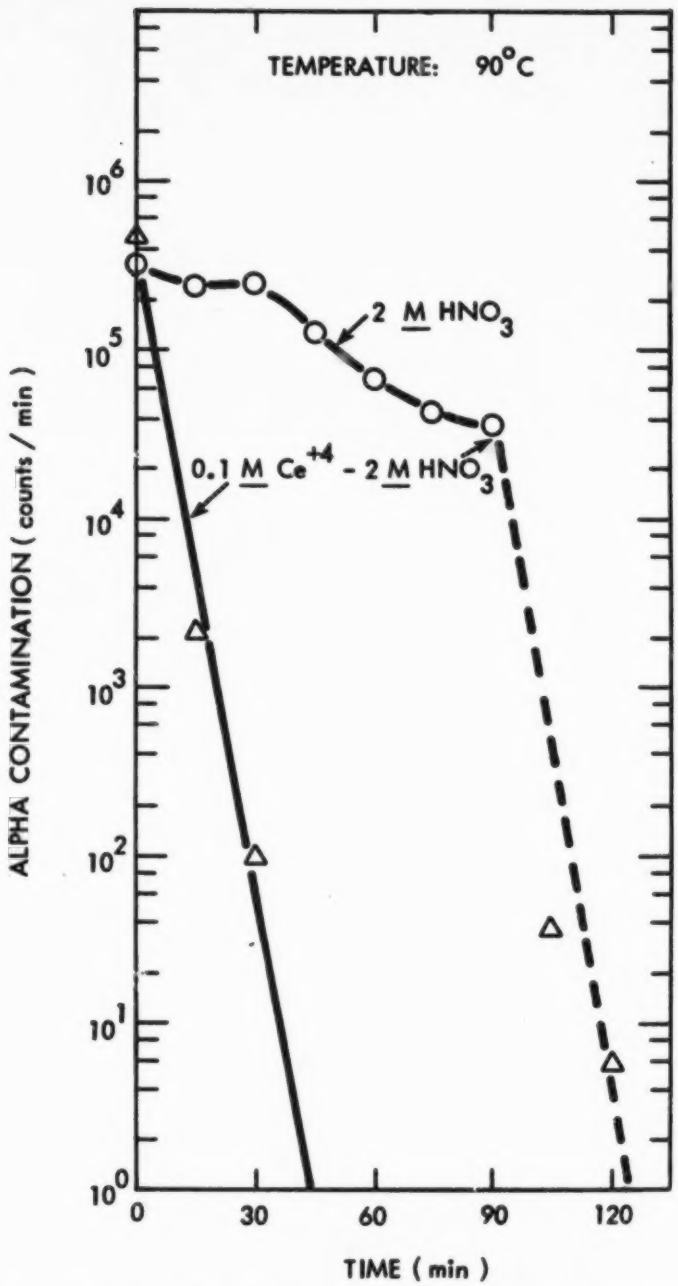

Figure 3.2. Effect of Ce(IV) on rate of decontamination of two similar stainless steel specimens.

O 2 M HNO_3 Δ 2 M HNO_3 with 0.1 M Ce(IV)

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- The process is more effective for irregularly shaped equipment than electrolytic decontamination methods.

- The process does not require immersion of the equipment to be decontaminated since a spray or flowthrough system could be used.

While this last point may literally be true, it would seem that, in practice, considerable complexity in the system might be required in order to achieve the sorts of temperatures and contact times needed for thorough decontamination.

3.3.4.3 Secondary Waste Streams From Chemical Treatment

No mention is made of specific components of the secondary TRU waste stream by either SRL or HEDL; however, the streams from both processes should be small. This is particularly true for the SRL process, where most of the actinide contaminants should be filterable, and the wash solutions, when spent, could be dealt with as low level waste. The filtered solid material would contain MnO_2 in proportion to the amount of reducing material encountered during the washing and other handling.

In the HEDL Ce(IV)-HNO_3 process, this reagent dissolves PuO_2 and other actinide oxides, so the actinides would be in solution, along with a relatively large amount of iron and the other constituents of dissolved stainless steel. Evaporation of the wash solution to recover HNO_3 would leave the actinides in a solid nitrate form, which could then be recovered if desired or calcined for incorporation of the oxides into a waste form such as glass or specially prepared concrete.

3.3.5 Decontamination of Nonmetallic Noncombustible Waste

While nonmetallic, noncombustible waste apparently does not lend itself to standard chemical treatments, and even though it constitutes a problem of lesser magnitude than that of metallic and combustible wastes, it cannot be ignored. For example, in decommissioning nuclear facilities, there may be an incentive to decontaminate certain metallic equipment for recovery, whereas structural material such as masonry and concrete will generally have no recovery value, yet will have to be decontaminated before the facility can be decommissioned. Also, if buried TRU waste should have to be retrieved and prepared for ultimate disposal, many large concrete items will have to be treated.

Certain types of incinerator, particularly the slagging pyrolysis incinerator, can handle a relatively high proportion of noncombustible material, including contaminated soil. However, they obviously cannot handle large concrete structures, and some other method must be used to deal with them. The approach taken in development work at PNL[21] is to attempt reducing the radioactivity level sufficiently to meet requirements by removing the contaminated surface layer. For this purpose a concrete spaller is being developed, which is capable of removing an 8-inch diameter section of concrete surface each time it is operated. Testing indicated that up to 100 ft^2/hr surface removal was feasible. In the first testing with Pu contaminated concrete, a floor surface was removed quickly without spread of contamination.

The use of very high pressure water streams was also being investigated.[21] A commercial unit demonstrated that the surface of a piece of typical Hanford concrete could be removed to a depth of 1/4-3/8 inch at a rate of 6 ft^2/min using about 1/2 gallon of water for each square foot of surface removed. Several problem areas will have to be investigated before the method can be properly evaluated. These include:

- dispersal of contamination and recontamination of cleaned surfaces,
- the question of whether contamination is driven deeper into the concrete, and
- removal of water from the contaminated rubble.

The secondary waste stream from treatment of concrete would appear not to be a problem. The most obvious immobilization method for concrete rubble would be incorporation into a specially prepared concrete (such as FUETAP) discussed in Section 2.5.2.

3.3.6 Status of Secondary Waste Stream Treatment

The aim of decontamination studies has been to develop processes that will reduce the level of contamination to below the 10 nCi/g TRU limit so that the material treated can be disposed of as LLW. The other requirement for a viable process is that the volume of secondary waste be both smaller than the original waste and in a form suitable for immobilization in a waste form meeting geologic disposal criteria. Most of the decontamination processes discussed under Section 3.3 generate secondary waste streams which meet the above requirements. Some of these waste streams have been mentioned in the text, and all are listed in Tables 3.8 and 3.9. In general, their volumes are much smaller than those of the original contaminated materials. The only process for which we have no conclusive evidence for a suitable secondary waste stream is electropolishing, and work on it is still under way at PNL.[26]

Considerable effort was put into developing a method of treating spent H_3PO_4. PNL evaluated a number of separation and purification methods, and carried out experimental work on several of those which looked as though they would be useful.[41,42] Ion exchange and solvent extraction were judged to be the most promising.

PNL rated the treatment methods more on the basis of electrolyte purification than optimization of secondary waste stream characteristics, and decided that ion exchange was the preferred method, with solvent extraction chosen as the backup technique. The ion exchange process was developed to the stage of testing a commercial acid purification unit with simulated cold spent electrolyte.[42] The unit performed well in terms of acid recovery and impurity (metal ion) reduction. However, no experiments were carried out with plutonium in the electrolyte at that time or in testing done at later periods when a full scale decontamination facility was being set up.[19,21,26] Because of this, the fate of plutonium in the process was not determined, though it was assumed that actinides would follow the stainless steel constituents.

The experimental work on solvent extraction, on the other hand, included work with Pu. Using methyl isobutyl ketone (MIBK) as the solvent, it was found

Table 3.8

Comparison of Electrolytic and Melting Methods for Decontaminating Equipment and Facilities

	Electrolytic Methods		Melt Slagging or Melt Refining
	Electrodecontamination	Electropolishing	
Temperature (°C)	70-90	Slightly above ambient	1500-1600[a]
Time required[b]	Few minutes	Few minutes	1 hour
Able to treat nonmetals	No	No	No
Adaptable to in situ use	Yes	Yes	No
Adverse factors	Poor throwing power	Complex handling of spent electrolyte and secondary waste stream	High operating temperature; possible high rate of crucible loss
Degree of decontamination and quality of product	Excellent decontamination; Roughened surface	Highly polished surface	Good decontamination factor but residual activity concentrated at the (much smaller) surface
Secondary waste stream:			
Composition	Sludge of actinide and ferrous metal hydrous oxides	Actinide and ferrous metal phosphates[c]	Borosilicate glass or other slag
Relative amount	Small	Small[c]	Larger than for other processes: approx. 1/4 of volume of original metal
State of development	Demonstrated on lab scale	Commercial[d]	Engineering scale

[a]For ferrous metals. Lower for Al and base metals, approximately the same as their melting points.
[b]For decontamination step only.
[c]Assumed from information available - secondary waste treatment not yet fully demonstrated.
[d]For pretreatment and decontamination steps only.

Table 3.9

Comparison of General and Chemical Methods for Decontaminating Facilities and Equipment

	General		Chemical	
	Liquid Honing	Vibratory Finishing	$Ce(IV)-HNO_3$	Others
Temperature (°C)	Ambient	Ambient	90	Ambient to >100 depending on reagent and application
Time required[a]	Few minutes	1 hour	1 hour	Few minutes
Able to treat nonmetals	To a reasonable extent	Yes	No	To a reasonable extent
Adaptable to in situ use	Yes	No	For some applications	Yes
Adverse factors	Difficulty of controlling dispersal of removed activity			
Degree of decontamination and quality of product	Good decontamination, usually to <10 nCi/g. Surface cleaned of oxides and extraneous material but not polished		Good decontamination, usually to <10 nCi/g. Surface roughened	Surface essentially unchanged
Secondary waste stream:				
Composition	Particles of metal, corrosion products, and abrasive	Corrosion products and extraneous material	Actinide and ferrous metal nitrates	Dependent on chemical agents
Relative amount	Small	Small	Small	Small
State of development	Demonstrated for treating single pieces by hand	Engineering scale	Demonstrated on lab scale (1979)	Engineering scale

[a]For decontamination step only. The time given can refer to treatment of individual pieces (e.g. liquid honing) or to relatively large batches (e.g. vibratory finishing).

that essentially all the Pu was removed from the electrolyte and rejected to the raffinate. While appreciable concentrations of Fe, Cr and Ni remained with the H_3PO_4, most of these constituents went to the raffinate with the Pu. The disadvantages of solvent extraction were said to be "its relative complexity, and possible safety considerations related to the use of organic extractants."[41] We feel it is debatable whether solvent extraction is any more complex a technique than ion exchange, and safety of solvent extraction processes is obviously not a big obstacle since they are used as standard methods for separation of kilogram amounts of actinides. Thus, it may be that solvent extraction will turn out to be preferred from the point of view of secondary waste streams, and ion exchange could be used as a backup to finish recovery of the H_3PO_4.

The bottom line is that either of the processes will probably be able to generate a suitable secondary waste stream containing actinide phosphates, but this has not actually been demonstrated.

3.3.7 Evaluation

Parameters and characteristics of the various methods for decontaminating facilities and equipment are summarized in Tables 3.8 and 3.9. The following observations can be made concerning them:

- All the methods work at least adequately and all except electropolishing have been demonstrated to produce acceptable waste streams of smaller volume than the original contaminated material.

- No one method is applicable to all materials and all situations, although vibratory finishing can be applied to most, aside from applications requiring in situ use. It has the advantage over electrolytic methods that it can be used for plastic and rubber components of contaminated facilities such as plutonium glove box lines. Experience has been that the presence of rubber and plastic pieces facilitates processing of the metal pieces.

- Vibratory finishing, especially with metal media, generates a very small secondary waste stream, as does electrodecontamination. Electropolishing probably will produce volumes quite a bit larger, though acceptable, as does melt slagging.

- Electrolytic methods and chemical cleaning can handle a wide variety of shapes and sizes which vibratory finishing cannot unless the equipment to be treated is first sectioned. The highly polished surface produced by electropolishing is advantageous for rinsing away contaminated electrolyte and for subsequent cleaning after reuse, when wiping is usually all that is required.

- Liquid honing can be used for almost any application, but in its present state-of-the-art is very tedious and causes excessive dispersal of the removed activity. In situ electropolishing methods (swab and pumped-stream) can handle any metallic surfaces that liquid honing can, but of course not nonmetallic surfaces. Application to remote handling has

been developed to some extent for in situ electropolishing, but not for liquid honing.

- Chemical treatment is effective for large bulky equipment (e.g. Pu glove boxes) and for remote treatment with liquid chemicals. Relatively small volumes of liquid are required. In situ swab electropolishing also uses small volumes of liquid since the liquid is recirculated.

- Melt-slagging uses a low ratio of slag/metal (approximately 0.1 on a weight basis) at each contact. If slag could be reused for several contacts with contaminated metal, the secondary waste stream would be kept very small. However, used crucibles would add greatly to the volume of the secondary waste unless their average service life could be lengthened. The principal disadvantage of the process is the high temperature required (up to 1600°C) which greatly reduces crucible life in addition to providing the usual complications of high temperature processes.

- Electropolishing and electrodecontamination appear to provide the most complete decontamination of the various methods, but of course are applicable only to metals with surfaces reasonably free from extraneous non-conducting materials. For metals, particularly ferrous alloys, they have the advantage that, with pretreatment such as vibratory finishing, pieces can often be cleaned to the point where activity is essentially undetectable. Thus, such material is not only no longer TRU waste, but could be either reused or recycled. It also should be noted that the electropolishing techniques developed by PNL were being used by two commercial firms as early as 1978 to provide decontamination services to nuclear facilities.[17]

- Melt slagging seems appropriate and efficient for handling scrap. When equipment is destined for reuse, obviously the other methods must be used. They may also be more efficient for dealing with material that can be readily sectioned.

3.3.8 Foreign Work on Decontamination

In November 1980, several U. S. DOE members connected with the TRU Waste Management Program took part in a workshop at Cadarache, France, attended by representatives from the nuclear waste management programs of the United Kingdom, West Germany, France, Italy and Belgium*. The workshop was concerned particularly with chemical washing of solid wastes, but other methods of decontamination were discussed. After the workshop, visits were made to French, German and British nuclear sites to observe and discuss decontamination operations.

It appears from the workshop and site visits that there are no important areas in which the European countries have better developed methods than the U. S. In most areas the U. S. has more highly developed methods, and most

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*Private communication from P. Hagan, DOE Transuranic Waste Systems Office, Rocky Flats Plant to D. MacKenzie, BNL, February 12, 1981.

effort in the European countries is currently being put into relatively simple methods involving treatment with chemicals (such as acids, bases and detergents). This is at least partly a result of the different classification of alpha-active waste and requirements for its disposal. For example, in the U. K. low levels of alpha activity are disposed of by shallow land burial, and levels above 20 mCi/m^3 (approximately 0.3 g $Pu\text{-}239/m^3$) by ocean dumping of the washed waste which has been shredded and placed in a 210-L drum with an overpack. The British do, however, have an active research and development program in more advanced decontamination methods, including five electrochemical processes, two of which apparently have not been investigated by DOE --electroerosion (surface passivation with abrasive removal of oxide) and electrocleaning (surface not dissolved, but contamination removed by microbubbles). The Germans also have done considerable work on electrochemical methods. Their more recent work has utilized the concentrated phosphoric-sulfuric acid and 60% H_3PO_4 polishing electrolytes. Although all their decontamination projects were successful, the electropolishing technology has not been extensively developed because of concern about the generation of large volumes of secondary wastes.

3.4 Miscellaneous TRU Waste Management Topics

Acid digestion as an alternative to incineration of combustible materials has been extensively developed by Westinghouse at their Hanford laboratories.[40,43-47] A method to dissolve refractory PuO_2 by treating with a HNO_3-$Ce(NO_3)_4$ mixture, thereby avoiding use of the very corrosive and dangerous reagent, HF, and addition of unwanted F^- to the process stream, has been developed at ORNL[48] and RFP.[49] Both processes have particular application to the actinide recovery aspect of waste management, but are also of interest to the waste disposal aspects.

3.4.1 Acid Digestion of Combustible Materials

In BNL's Task 2 Interim Report[1] it was recommended that combustible TRU waste not be allowed in repositories. The usual way of converting combustible waste to an inorganic form is to incinerate it. The resulting incinerator ash is in a form which can be immobilized in an acceptable matrix such as glass or ceramic, and at the same time its volume has been greatly reduced from that of the original waste.

Another method of treating combustible waste is by acid digestion. This method, apparently originally tested on TRU waste in Sweden, has been developed by Westinghouse at their Hanford Engineering Development Laboratory (HEDL) to the point where it is anticipated that it will be used in a production unit to treat Hanford combustible TRU waste and scrap.[43,44] The chemical processes involved are dehydrogenation and/or dehydration of the organic material by concentrated H_2SO_4 at 250°C, followed by oxidation of the resulting carbon to CO_2 with HNO_3.

Development of the acid digestion process began at HEDL in 1972. The process progressed from initial 1-L to 5-L laboratory scale experiments to 200-L operations conducted in a spherical glass digestion vessel contained in a

nonradioactive pilot plant called the Acid Digestion Test Unit (ADTU).[45] Testing in the ADTU confirmed the feasibility of the process and revealed the following advantages and disadvantages of the system:

Advantages

- The system handled a wide variety of waste materials, including leaded gloves and certain unique wastes not readily adaptable to incineration.
- Chemical reactions are readily controlled by adjusting the waste and nitric acid feed rates or the digestion temperature.
- The process occurs at low temperature, which allows retention of plutonium in a water soluble, non-refractory form.
- Generation of tars, soot, and flyash is avoided.

Disadvantages

- Processing rates are relatively low.
- Construction materials are limited.
- The presence of a neutron moderating liquid limits the design options and plutonium inventory required to meet criticality safety standards.

The next stage of development was the construction and operation of a radioactive demonstration plant called the Radioactive Acid Digestion Test Unit (RADTU) to demonstrate the processing of combustible TRU waste from Hanford's Z-plant. Starting in November 1978, RADTU operated on a two-shift-per-day basis, five days/week for six months, processing 2100 kg of waste during the period.[43]

To increase the capacity of the unit from 3 kg/hr to approximately 10 kg/hr, a new high rate annular digester was installed in September 1979, with associated equipment to improve processing.[44] The new digester design provided more intimate waste-acid contact and improved heat transfer, and also allowed a much higher inventory of fissile material in the digester. The new unit began processing low level waste from the Z-plant in June 1980, with the intention of gradually increasing the plutonium levels in the waste as operating experience was gained. Processing of recoverable scrap was expected to begin in the first quarter of FY 1981.[44]

Residues for actinide recovery or for disposal are obtained by 350°C evaporation of the H_2SO_4, which is recycled. Methods of recovering plutonium from the acid-digestion residues have been developed.[47] This plutonium is nearly all in the form of $Pu(SO_4)_2$, which, although quite insoluble in H_2SO_4, is soluble in HNO_3. The key steps developed for the recovery process involve leaching of the residue with 7M HNO_3, filtration to remove undissolved material, and anion exchange to concentrate and purify the plutonium. The product can be converted to PuO_2 by oxalate precipitation and calcination. Losses due to Pu not leached out of the residue were generally

less than 1%. Washing of the oxalate precipitate caused losses to the filtrate of 1.5%.

Preparation of residue for disposal involves drying at 350 to 400°C. The resulting dry cake or powder consists essentially of sulfates of Fe(III), Al, Ca, etc., which can be converted to oxides by calcining at suitable temperatures. There appears to have been no work done on immobilization of actual TRU contaminated residues - normal procedure was to store (for future Pu recovery or eventual disposal) the steel pots in which the residue had been prepared.[44] However, before RADTU began operating on radioactive waste, a demonstration using inactive acid-digestion residues showed that these were completely suitable for use in a borosilicate glass making process,[46] even though they were much higher in iron than later residues. Impact testing of glass samples showed excellent mechanical durability.[47] Leach testing of the glasses gave an average leach rate of 2×10^{-5} g/cm^2-day in 14-day static distilled water tests,[46] a result which was fairly well in line with those for many HLW candidate glasses at that time.

Thus, the acid-digestion process can be directly applied to disposal of TRU waste. Although its main purpose is for recovery of actinides, it has been demonstrated with waste containing actinide levels well below the 5 g/kg waste level for recovery[50] but well above the 10 nCi/g TRU limit. Teflon appears to be the only carbon containing material not digested. The method has worked well for almost everything combustible except volatile liquids such as waste solvent streams from solvent extraction processes. Also certain unique wastes which would be almost impossible to handle by incineration have been shown to be readily acid-digested and these might well be worth processing for disposal in this manner (even though the actinide content might not be high enough for economical recovery) simply to obtain a suitable waste form.

3.4.2 Dissolution of Refractory PuO_2

In an earlier section (3.3.4.2) the chemical decontamination of stainless steel by Ce(IV)-HNO_3 solutions was described. Although the principal reason for use of this reagent was its relatively rapid dissolution of a surface layer from the metal, another important factor was its known ability to dissolve refractory PuO_2. Because of this ability, the Ce(IV)-HNO_3 system was chosen for two different studies of ways to treat wastes containing refractory actinide oxides.[48,49] In the reports of the studies, neither group of workers made reference to the work of the other, but both groups arrived at very similar conditions for operation of the process. For example, both groups settled on 0.1M Ce(IV)-4.0M HNO_3 as the standard leach solution, 100°C (or reflux temperature) as the temperature required for dissolution, and 1A as the current for electrolytic regeneration of Ce(IV) from Ce(III).

The RFP study[49] was carried out as part of a program undertaken by ORNL to develop a cost-risk-benefit analysis of actinide partitioning and transmutation as a waste management concept.[51] Its purpose was to provide information to the program regarding the partitioning aspects.

Incineration had been chosen as the reference process for treating combustible wastes. This treatment leaves plutonium and americium in the form of refractory oxides which are very difficult to dissolve and which are

partially occluded by other oxides in the waste such as SiO_2. A standard method of recovering the actinides had been to treat with boiling $HF-HNO_3$ mixtures, but this very corrosive dissolving agent, and the presence of $HF-SiF_4$ vapors in the off-gas system were big disadvantages. It was known that Ce(IV) in the presence of strong HNO_3 could solubilize PuO_2, but with continuous addition of Ce(IV) to oxidize carbon in the ash the cerium content would soon build up to the point where it would have to be reprocessed. The method as developed by RFP kept cerium in the Ce(IV) state by anodic oxidation with electrodes in the dissolver solution, so that no addition of Ce(IV) was required.

Advantages of the $Ce(IV)-HNO_3$ system over the $HF-HNO_3$ system are:

- cerium can be recycled whereas $HF-HNO_3$ must be replaced frequently,
- corrosion and off gas problems are less severe, and
- silica is neither solubilized nor volatilized.

The $Ce(IV)-HNO_3$ system has several major advantages over methods involving fusion of ash, including operation at temperatures not much above 100°C, as opposed to 900°C for fusion. The main disadvantage of $Ce(IV)-HNO_3$ is that SiO_2 is not solubilized to release small amounts of trapped PuO_2, so that quantitative recovery of Pu is not achievable without secondary treatment.

The other study, by ORNL,[48] was concerned with removal of PuO_2 from used HEPA filters only. Since the PuO_2 was on the surface of the glass filter fibers, rather than partially occluded by SiO_2 or silicate particles as in the RFP investigation, no problem was encountered in achieving complete solubilization. The study, therefore, concentrated on several problems associated with the filters themselves, such as pretreatment to get rid of carbonaceous material, and separation of the leach solution from the gel-like mass of glass fibers. In order to achieve this separation, the filter media were treated in a packed column in which they rested on a porous plate. The leach solution was expelled from the column back to the electrolysis cell by applying a small excess air pressure.

The title of the ORNL report[48] uses the term "recovery," and indeed the process would be recovery if the HEPA filters contained sufficient Pu to be classed as recoverable. However, if lesser amounts of Pu were involved, the process could be considered as a method of decontaminating HEPA filters which could not be handled by some of the incinerators used for combustible TRU waste. In this case the method has a definite place in any type of TRU waste disposal strategy. In the case of the incinerator ash treatment developed by RFP,[49] it seems that recovery of actinides would constitute the only reason for leaching the ash, unless partition-transmutation was a requirement of the U. S. waste management strategy.

3.5 Conclusions

Even as late as 1978 when the DOE report "Technology for Commercial Radioactive Waste Management"[52] was in preparation, densification by compaction and melting was seriously considered as the standard method of preparing contaminated metal wastes for disposal. It had been shown at PNL (then BNWL) that when contaminated metal was melted under an inert atmosphere the radioactivity could

be dispersed and fixed in the solidified metal.[28] However, as pointed out in Section 3.1, even if the relatively large volumes of compacted or melted metals could be tolerated, partial decontamination will often be necessary so that dismantlement can be carried out. It seems worthwhile, then, to carry the process one step further and consider decontamination as a preferred disposal method.

The arguments for decontaminating cladding hulls and failed and decommissioned equipment are essentially the same. If activity level can be reduced below the TRU limit, which currently is 10 nCi/g, it will be non-TRU waste suitable for shallow land burial. In other words, the entire retrievable storage process with its attendant costs, hazards, and increased (rather than decreased) waste volume can be eliminated. That this should be readily achievable in most instances is supported by the examples, cited in previous sections of this chapter, of decontamination procedures which reduced TRU contamination to well below 10 nCi/g, and often to a level undetectable by routine radioactivity survey methods. This latter degree of cleanliness would permit reuse of equipment, and, in the case of scrap, might allow recycle of some metals within the nuclear industry.

The case for treating TRU contaminated material by decontamination, rather than by retrievable storage followed by later exhuming and processing for geologic disposal, is summarized in Table 3.10 as excerpted from a PNL report.[19]

Table 3.10

Comparison of TRU Waste Treatment by Decontamination
Versus Retrievable Storage/Geologic Disposal

Retrievable Storage/Geologic Disposal	Decontamination to Produce Non-TRU Waste
Remove contaminated component	Remove contaminated component
Load into storage box	Transport to decontamination facility
Transport storage box	Disassemble/section
Store/monitor for 20 years	Pretreat/decontaminate
Exhume box	---
Transport to repackaging facility	Non-TRU waste - final disposal by convenient shallow land burial
Unpackage deteriorated waste	
Disassemble/section waste	
Process waste	
Repackage for geologic disposal ←	Prepare small amount of secondary waste for geologic disposal
Overpack for transport	
Transport to disposal site	
Final disposal	
Amount of TRU Waste for Disposal	**Amount of TRU Waste for Disposal**
At least double the initial amount	Small fraction of the initial amount

In our view, decontamination technology is in a well developed state in this country. A great deal of effort has been put into both research and development in the last few years, with very good results. The electropolishing method had even reached the stage of commercial use in 1978.[17] Work in European countries parallels to some extent that being done in the U. S., but specific goals are different since there are fewer constraints on disposal of alpha-contaminated wastes and more varied disposal options. Thus, efforts tend to be concentrated on chemical treatments rather than on the more advanced methods being developed in the U. S. However, because waste storage space in most European countries is very limited, the more advanced methods, which can decontaminate equipment for reuse, should soon receive wider attention there.

On the basis of our review of the U. S. programs it can be concluded that a number of very good decontamination methods have been developed, which should be adequate to handle any application likely to arise. They have all, with the exception of liquid honing, been shown to work satisfactorily on a reasonably large scale. The secondary waste streams from most of the processes are small and suitable for waste form preparation. However, this has not been shown to be true for the electropolishing process - although the methods proposed are said to be well known, the ability to recover the TRU contaminants from the spent H_3PO_4 electrolyte in a small volume suitable for disposal has not actually been demonstrated. Further R&D must be carried out to clear up this point before electropolishing can be considered satisfactory from all aspects. Further development is also required for the liquid honing method if it is to be a useful addition to the list of applicable decontamination processes. The most pressing requirements are an effective means of containing the radioactive material removed by the process, and the design of equipment which can decontaminate relatively large areas in a reasonable time. Adequate containment is essential for any method, and relatively high rates of contaminant removal would be required for large scale decommissioning work where the in situ devices would probably have their greatest application.

While a number of processes for decontaminating facilities and equipment have been developed to a high degree of reliability in the U. S. program, the situation with respect to management of cladding hulls is less satisfactory. While the Swedish process is operating on a full plant scale, work on development of the U. S. proposed methods was stopped before any of them could be demonstrated on an engineering scale. The available information indicates that demonstration of one or more engineering scale processes could be accomplished fairly readily. The necessary development work should be done soon in order to prepare for the advent of commercial fuel reprocessing.

As pointed out in Section 3.2.5.3, the U. S. approach of decontaminating to produce non-TRU waste suitable for low level waste disposal is entirely appropriate as long as the volume of the secondary waste streams is much smaller than that of the original hulls. As regards the PNL decontamination-densification process, the moderate temperature eutectic melting method being developed by the French should be considered as an alternative to the high temperature melting of Zircaloy for the densification step.

The philosophy behind DOE's decontamination strategy as given in Table 3.10 is laudable and it should definitely be put into practice. However, to require

DOE to implement it, e.g. by refusing to accept metallic waste for geologic disposal, is probably not justifiable. This conclusion is based on the following considerations.

There is nothing in the Federal Register version of 10 CFR 60[53] which would prevent metallic wastes from being accepted in a geologic repository. The only requirement in 10 CFR 60 which might exclude it is in Section 60.111(c)(3)(ii) which limits the TRU release rate from the engineered system. Since essentially all the TRU activity in TRU metallic waste is surface contamination or material in cracks, bolt holes, etc., it would be subject to removal, or release, from the metal as soon as the expected conditions of repository flooding and container breaching occurred. Depending on its chemical form (soluble compound, relatively insoluble oxide, colloidal dispersion, etc.) the release rate from the underground facility could potentially be very much higher than 10^{-5} per year. We consider that it would be very difficult for DOE to guarantee the chemical form of the TRU activity, and it might instead prefer to implement its decontamination strategy. That would certainly make sense, since the strategy is technically sound, it is economical, and the methods are in place. However, the decision presumably is DOE's; since NRC sets criteria on the basis of risk to health and safety rather than economy, it does not appear justifiable for it specifically to exclude metallic wastes from repositories.

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4. GAS GENERATION

4.1 Introduction

This section of the report dealing with the potential for evolution of toxic and/or explosive atmospheres within the waste package or emplacement room is an expanded and updated version of the Interim Report.[1] The information discussed in this section derives from R&D activities conducted in support of WIPP. This data has been reviewed for its pertinence to the disposal of commercially generated TRU waste in a licensed repository.

For the purpose of evaluation in the Interim Report, the applicable proposed criteria and regulations from the seventh draft version of 10 CFR 60 were addressed.[2] Since the Interim Report was issued, NRC's Advance Notice of Proposed Rulemaking for regulating geologic disposal of HLW was published in the Federal Register.[3] Several important differences in definition and criteria exist between draft 7 and the Federal Register version of 10 CFR 60. The evaluations conducted in this report will continue to address the "strawman" criteria in draft 7 and the pertinent definitions, criteria, and regulations detailed in the Federal Register version of 10 CFR 60. The proposed rules of immediate importance to this section of the report and which form the basis of the evaluation are given in §60.133 of 10 CFR 60.[3]

Most, if not all, of the research and development (R&D) activities conducted in support of the WIPP acceptance criteria are now complete or have terminated. It is felt that no new significant information will be generated in the near future that has direct bearing on the development and support for NRC regulations and criteria pertaining to the allowability of combustible organic transuranic (TRU) waste or other gas producers in a licensed repository. This situation may change as data become available from in situ experiments planned at the WIPP site. Thus, the review, evaluation, conclusions and recommendations contained in this section complete the BNL evaluation of gas generation in a waste package or repository.

4.2 Purpose and Scope of Evaluation

A key responsibility of NRC is the evaluation of all aspects of the geologic repository performance which could affect the public health and safety. In this context, an assessment of the performance of the waste package in a mined geologic repository is required. One important process that could affect the long term isolation behavior and safety of a licensed repository is the potential evolution of toxic and/or explosive atmospheres within the waste package or emplacement room. Thus, it is the purpose of this section to discuss the results of recent programs that are concerned with potential gas generation from commercially generated TRU contaminated wastes and to show how and whether the information can be used to support proposed regulatory criteria.

About 98% (by volume) of the TRU waste produced in DOE installations is classified as contact handled*. This includes approximately 54,000 m^3 of contact handled waste retrievably stored at the Idaho National Engineering

*Waste packages with surface dose rates no higher than 200 mR/hr are designated contact handled TRU waste.

Laboratory (INEL), the Rockwell Hanford Operations (RHO), the Los Alamos Scientific Laboratory (LASL), and the Savannah River Plant(SRP).[4] Of the 54,000 m^3 of TRU waste, about 75% (v/v) is stored at INEL. Some of the characteristics of TRU waste at INEL[5,6] and LASL[7] have been evaluated.

Approximately 20 to 25% of the waste by volume in retrievable storage at INEL is combustible.[8] In addition, a sizable fraction of the organic, combustible TRU waste is susceptible to production of gas by various degradation mechanisms. The combustibility and potential dispersibility of the waste is an important factor during the operational phase of the repository while the tendency to produce gas is important to the long term repository behavior. The acceptability of this non-processed waste, in terms of its potential for gas generation and the consequences thereof, will be considered in this study.

The evaluation of possible gas generation situations within a repository requires careful consideration of several areas. The Department of Energy (DOE) has been conducting research in the area of TRU waste management, the purpose of which is to provide technical support for the development of waste acceptance criteria for the deep geologic terminal isolation of transuranic wastes in a bedded salt repository. The scope of this review and evaluation of the available information on gas generation from the DOE program includes the mechanisms responsible for gas generation and how they are affected by various parameters, quantities and identification of gases produced, consequences of gas generation, conclusions drawn from the results, and how the information addresses proposed regulatory criteria. Recommendations based on the evaluation will be given below.

4.3 DOE Assessment

The most extensive experimental information regarding the potential for gas generation from TRU wastes was sponsored by the Department of Energy. The results of this program have recently been reported.[9-12] A comprehensive review of all applicable waste degradation-gas generation data for TRU wastes was the subject of two of these reports.[10,11] They provide a summary and interpretation of these data from research over the past several years. The information and references therein are discussed below. Any new information that has been made available to us since publication of the Interim Report[1] has been included in the assessment. Topics discussed in the subject reviews[10,11] included gas generation rates from several TRU waste forms, degradation mechanisms, synergistic effects on mechanisms, composition of the gases produced, methods for reducing gas production rates, and comparisons of the modes of gas generation.

Mechanisms which result in gas generation from the degradation of existing and potential forms of defense related TRU waste matrices and containers along with the primary participants in the DOE/Sandia program are given in Table 4.1. Experimental investigations of gas generation from degradation of TRU waste have

Table 4.1

Waste Degradation Mechanisms and DOE Program Participants

Mechanism	Investigating Laboratory
1. Radiolysis	Los Alamos (LASL) Savannah River Laboratory (SRL)
2. Thermal and Catalyzed Thermal	LASL, SRL
3. Chemical Corrosion	Sandia (SLA)
4. Bacterial	LASL University of New Mexico (UNM)

also been conducted at the Rocky Flats Plant (RFP). The conditions under which some of the experiments were conducted are environmental conditions anticipated to be present at the WIPP TRU waste storage horizon in the repository. Two of the more important parameters (and ranges of interest) that may affect gas generation rates in the repository are (1) temperature (20° to 100°C) and (2) pressure (0.1 to 15 MPa). Other factors considered for their influence on degradation and production rates were aerobic versus anaerobic conditions and the geochemical environment. The TRU waste matrices of primary interest are cellulosics (paper, cotton, cloth, wood, etc.) plastics (polyethylene, polyvinyl chloride), rubbers (neoprene, Hypalon), a composite of the above organic matrices, concrete-TRU ash, process sludges, and asphalt. For purposes of assessment and comparison of gas generation rate versus degradation mechanism, representative TRU waste characteristics were defined to approximate the waste in temporary storage at INEL.[8] These characteristics are summarized in Table 4.2. The curie amounts listed in parentheses in the last column of Table 4.2 are not what is expected based on a specific activity of 0.070 Ci/g for weapons grade plutonium (94% Pu-239 and 6% Pu-240). Shefelbine gives a more detailed listing of the isotopic composition of weapons grade plutonium.[8] From the specific activity listed there, it would appear that Molecke[11] has assumed that the ^{wg}Pu composition is dominated by Pu-238, -239, and -240. For the sake of accuracy, the data from Table 2 of reference 11 have been reproduced as published.

The pertinent data from the available information on gas generation from various waste matrices are summarized in Table 4.3. G values (defined as the number of gas molecules formed/100 eV of absorbed radiation) are a measure of the efficiency of radiation induced processes. Here, they refer to the total number of gas molecules formed for the drum characteristics listed in Table 4.2. In the calculation of gas generation rates (as moles/yr/drum), pressure, temperature, and dose rate effects were not considered. Also, all the alpha decay energy was assumed to be deposited in the waste matrix.

4.3.1 Environmental Conditions

We initially assumed a maximum credible temperature range experienced by TRU waste to be 40-50°C.[1] A recent calculation indicates that a salt repository

Table 4.2

Assumed Characteristics of Standard Drum (210 Liter, Mild Steel) Content
(Data taken from Table 2 of Reference 11)

Waste Material	Matrix Weight (kg)	Contamination (g ^{wg}Pu)[a]
Cellulosics	51.4	0.5(0.039 Ci)[b]
Plastics	51.4	0.5
Rubbers	51.4	0.5
Organic composite	51.4	0.5
Organic setups (solidified oils)	190	0.5
Process sludges (first stage)	190	(89)(6.9 Ci)
Polyethylene liner	8.6	
Mild steel drum	25	
Concrete-TRU ash	300	200(15.4 Ci)
Asphalt	135	100(7.7 Ci)

[a] ^{wg}Pu = weapons grade plutonium.
[b] Specific activity of ^{wg}Pu = 0.070 Ci/g.

containing only TRU waste will not experience an appreciable temperature change (Figure 4.1).[13] The repository temperature is important since leaching mechanisms and many of the waste degradation mechanisms can be accelerated due to an increase in temperature. Based on these calculations, the temperature of a TRU waste-containing salt repository will not likely exceed 30°C after closure. A temperature range of 25-30°C is certainly more realistic than 40-50°C.

4.3.2 Radiolytic Gas Generation

4.3.2.1 Cellulosics

Combustible cellulosics are a sizable component of the existing TRU inventory. This, plus the fact that cellulosics, polyethylene,[14] and polyvinyl chloride (PVC)[15] evolve more gas than other existing waste types, has resulted in much experimental information on the radiolytic degradation of this organic matrix. At the same time, significant uncertainties and discrepancies have arisen in the experimental results. The most extensive research effort in the areas of radiolytic and thermal degradation of cellulosics has been carried out at LASL, with additional work having been conducted at SRL and RFP. The variables investigated at LASL for their effect on gas generation were:

(1) Waste matrix (see Table 4.3).
(2) Dose rate (expressed either as plutonium concentration in the waste matrix or contamination level/drum) - 0.1X to 160X (1X = 4 x 10^5 nCi/g which corresponds to 200 g of ^{wg}Pu in a 210-liter drum containing 34 kg of combustible waste).

Table 4.3

Radiolytic Degradation Data Summary for TRU Waste Contaminated Matrices[a]
(This is essentially an updated version of Table 3 in Reference 11)

	Matrix[b]	G(Total Gas)[c]	Moles/Yr/Drum
LASL	Cellulosics	1.9 (20)	0.0073
	PVC	1.0-10 (20)	0.0039-0.039
	Asphalt	1.4 (27)	1.1
	Cellulosics, Dry	1.6 (14)	0.0062
	Cellulosics, Wet	1.5 (14)	0.0058
	Composite	1.4 (14)	0.0054
	Polyethylene	2.6-3.2 (20)	0.010-0.012
	Pump Oil	1.3-1.8 (14)	0.0050-0.0069
SRL	Cellulosics (22°)	1.9 (21)	0.0073
	Pump Oil	2.7 (21)	0.010
	Octane	4.5 (21)	0.017
	Concrete-TRU Ash	0.00030-0.66 (30,31)	0.00046-0.98
RFP	Cellulosics, Dry	0.63 (17)	0.0024
	Cellulosics, Wet	0.31 (17)	0.0012
	Polyethylene	0.73 (17)	0.0028
	PVC	0.43-0.96 (17)	0.0017-0.0037
	Plexiglas	1.9 (17)	0.0073
	Rubbers	0.37 (17)	0.0014
	Oil	3.1 (17)	0.012
	Ion Excnange Resins	0.11 (17)	0.00042
He Generation (from alpha decay)	(0.5 g ^{wg}Pu)		3.7×10^{-8}
	(200 g ^{wg}Pu)		1.5×10^{-5}

[a]Unless otherwise noted, temperature conditions were:
20° (LASL)
23° (SRL)
STP (RFP)
[b]Average content of weapons grade Pu per drum listed in Table 4.2.
[c]The numbers in parentheses are the references from which the G values were taken.

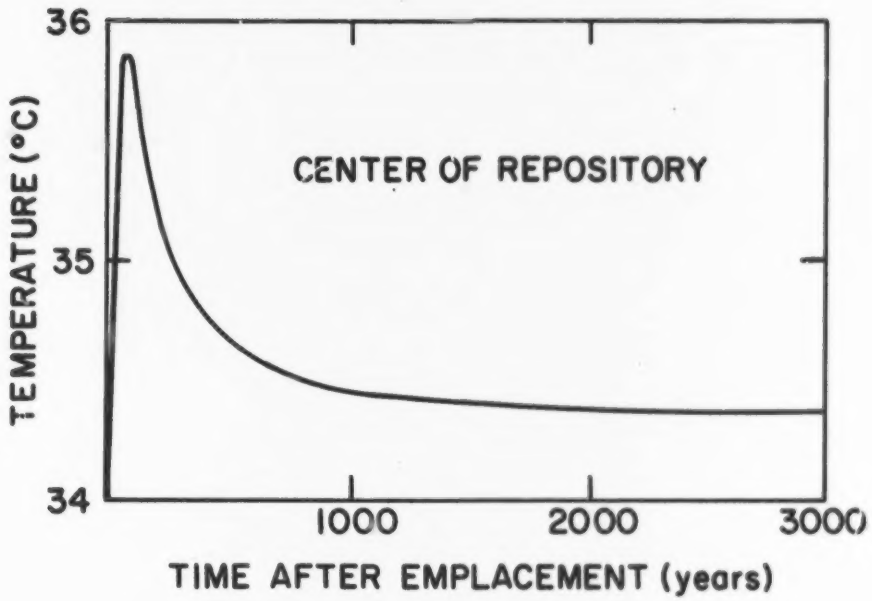

Figure 4.1. Long term temperature response of the WIPP repository. (This is Figure 9-15 of Reference 13).

(3) Temperature - 20°, 40°, 70°, and 100°C.
(4) Time - from one week up to four years.
(5) Pressure - 101 to 1.45 x 10^4 kPa.

The important results from the radiolytic gas generation studies involving cellulosic waste matrices are given below:

(1) It should first be noted that the G values from LASL and SRP for celiulosics and pump oil are in fairly good agreement with each other while those from RFP do not agree. Possible explanations for these discrepancies are discussed below.

(2) G°(gas) (the G value for gas formation at t=0) from alpha radiolysis is independent of the quantity of contaminant radionuclide present. This result experimentally confirms the assumption that alpha radiolysis of cellulose is not dose rate dependent. Data from LASL indicated that, in the case of cellulosics, G°(gas) was 2.9 for dose rates $\leq$40X and 1.3 for dose rates of 80X and 160X.[15] It was felt that the anomalous discontinuity in G°(gas) between 40X and 80X may be due to a rapid decrease in G(gas) at the higher dose rates that was not observed during periodic gas sampling.[16] The anomalous behavior prompted the LASL group to repeat some experiments at 40X and 80X dose rates using

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more sensitive pressure measuring equipment that provided continuous monitoring and an inert argon atmosphere that eliminated any complications due to oxygen depletion.[14,17] The results of these experiments showed that the initial gas generation rate for the argon atmosphere (40X dose rate) experiment gave a G°(gas) of 2.0 to 2.4, some 40 to 50% higher than the G°(gas) in air.[18] It is further noted that the experimental value of G°(gas) for an air atmosphere is significantly lower than the value resulting from an extrapolation through a total dose region where no data existed.[15] This indicates that oxygen depletion is slow for this dose rate and yields lower G(gas) values than for the comparison argon atmosphere experiments. An inert atmosphere experiment conducted at a dose rate of 80X gave a similar value of G°(gas) as for the 40X experiment.[19] A value of G°(gas) of 1.9 has been reported by LASL for a dose rate of 160X, but it was not stated if this was under inert atmosphere conditions.[20] Since previous results gave a value of G°(gas) = 1.3 in air for this dose rate, it must be assumed that the value of 1.9 is for argon atmosphere conditions. Thus, based on experiments performed under inert atmosphere conditions over a four-fold range of dose rates (40X to 160X), the LASL group has concluded that G°(gas) for alpha radiolysis of cellulosics is not dose rate dependent. Based on results from SRL,[21] the same conclusion has been reached concerning the dose rate dependence of cellulose degradation. Given the uncertainties inherent in this type of experiment (some of which are discussed below), the replication in results that has been observed,[19] and the presence of oxygen in the SRL experiments, it is probably safe to say that SRL and LASL are in reasonable agreement on the issue of dose rate dependence.

(3) G(gas) decreased with increasing total dose for dose rates (i.e., Pu loadings) that ranged over a factor of 1600. For reasons discussed in (2) above, the original data from LASL suggested that although G(gas) decreased with time, the decrease was slower for the lower dose rate experiments than for the higher dose rate experiments.[15] These data also indicated a higher G°(gas) for dose rates <40X. The more recent results on alpha radiolysis of cellulose [see (2) above] reveal that all G(gas) versus dose data fall on the same curve regardless of dose rate. The decrease in G(gas) with time is attributed to localized matrix depletion, i.e., the short range of alpha particles results in material depletion in the immediate area of the radionuclide contaminant. Similar behavior in G(gas) was observed at SRL.[21] The effect in this case was claimed to be due to formation of products that produce less gas as the radiation exposure progressed. What the nature of these products (other than H_2, CO, or CO_2) might be and how they could "produce" less gas was not discussed. The results from RFP have shown that, in agreement with LASL and SRL, gas generation rates decreased as a function of elapsed time.[17]

(4) Compositions of radiolytically generated gas were determined mainly by mass spectrometry. There is good agreement as to the identity of the gases generated.[14,16,17,21] The major gases produced are hydrogen, carbon dioxide, and carbon monoxide in the approximate mole percent ratio of 1.0/0.43/0.22. The composition of the evolved gases was found

to be independent of dose and dose rate,[7,15,16,18] even though G(gas) decreases with increasing dose. The proposed explanation for this is that when an alpha particle is effective in producing gas, it damages the cellulosic polymer in the same manner each time, but the number of effective collisions decreases because of matrix depletion.[18]

At this point, a discussion of some of the results and discrepancies in these results for cellulosics is in order. The LASL data would seem to indicate that the initial G values for cellulosics are the same regardless of whether the material is wet or dry.[14] Water does undergo alpha radiolytic decomposition,[22] so this would suggest that water sorbed by the cellulose would affect gas production. The value of G° = 1.6 (LASL, Table 4.3) is for a dose rate of about 50X while that of 1.5 is for a dose rate of about 25X. Thus, the rates of gas production are similar for a difference of two in contaminant loading. In addition to the increased rate of gas generation for wet cellulosics, the fraction of H_2 produced increased from 50 to 80%. The G values (not G° in this case) obtained at RFP are lower than those from LASL and SRL but, more importantly, the gas yields for wet cellulosics are lower than for dry for dose rates comparable to those used at LASL.[17] Although the cellulose-water system may not be completely understood under these conditions, the RFP results are surprising in view of the large amount of water reportedly present in the RFP samples and the effect of dose rate in aqueous systems.[22,23]

Possible explanations for the lower G values from RFP have been offered.[11] The G values reported by Kazanjian (RFP)[17] were determined from the slopes of graphs of the gas produced versus time after the oxygen had been depleted. Thus, they are not G° values and may be a measure of the rates after significant matrix depletion had occurred. Even if the RFP data had been extrapolated back to time t=0, recent LASL results[18,19] indicate a lower G° value is obtained for dose rates comparable to those of RFP (approximately 70X) if oxygen is present. However, the variability in the conditions under which these experiments were performed necessitates that the intercomparisons made among the results from the three laboratories be viewed cautiously. The rate at which the total gas pressure changes during degradation depends on several variables, including, in this case, the rate at which oxygen is consumed. If oxygen is consumed at a rate that is negligible compared to the hydrogen production rate, for example, then the G values measured from the initial rate of production are truly G° values. This is not the case as the oxygen depletion rate becomes comparable to the production rate. In the case of the SRL results,[21] G° values were measured from experiments that were not conducted for more than 100 hours. The extent and rate of oxygen depletion after such a short observation time could not be evaluated due to a lack of data indicating the contamination level of the cellulose matrix. Thus, in view of the behavior of this system under aerobic conditions, it would appear fortuitous that the G° values for cellulosic degradation reported by LASL and SRL are in such good agreement.

Another concern is the depletion of the waste matrix. For particles of high linear energy transfer such as alphas, the rates of gas production from degradation are dependent on the amount of energy absorbed by the material. The greater the range of the alphas in the material, the greater the extent of degradation. Kazanjian recognized this fact but stated it in contradictory terms.[17] He concluded that for contaminant particles larger than 30 μm (PuO_2 in this case), the depletion times would be on the order of a few months, and for particles on the order of atomic dimensions, the material would never be depleted. As the PuO_2 particles increase in size, more of the alpha energy is absorbed by the contaminant and less is available for gas generation. This implies that depletion times should be longer, not shorter as suggested by Kazanjian, for larger particle sizes. Experimental results on TRU contaminated concretes from SRL are in contrast to those from RFP as regards particle size,[24] i.e., $G(H_2)$ from the alpha radiolysis of water decreased as the size of the PuO_2 particles increased. Some points regarding the reliability of data and interpretations based on matrix depletion were made by Kazanjian.[17] If the rates depend on depletion of material, then movement of contaminant particles can increase or decrease the rates.[14,17] A non-uniform dispersion of particles throughout the matrix can result in similar behavior due to increased alpha flux within a given volume. It has been stated that gas volumes generated by alpha radiolysis depend on contaminant particle size and distribution.[14] However, no corroborating evidence is apparent in support of this conclusion except for a comment on the possible dispersion of Pu-238 contaminant in a drum that was generating significant amounts of hydrogen. Other disconcerting results from RFP involved an anomalous dose effect. Wastes loaded with Pu-238 had a dosage about 200 times greater than the same wastes loaded with Pu-239. As Kazanjian noted, under similar experimental conditions, the Pu-238 should have been more effective in gas generation but the results did not strongly support the predicted behavior.

(5) A synergistic enhancement of gas generation was found with increased temperature. Upon going from 20° to 55°C, the gas production rate increased by 43%.[14] Other data have shown that, for a 50°C increase in temperature (from 20° to 70°), the gas evolution rate initially increased by 70% and then diminished to 20 to 40% higher with increasing dose (time).[18] No discernible trend was observed with increasing dose. The higher temperature experiments continued to produce more gas even at long exposure times. The synergistic effect decreased with time but apparently did not disappear completely.[16] It had been anticipated that this effect might diminish with exposure time due to enhanced matrix depletion resulting from thermal degradation. This observation would seem to support the conclusion (see below) that matrix depletion due to thermal degradation is quite small at 70°C. It would appear that considering the conditions under which the thermal effect experiments were conducted (160X dose rate), a pressure increase has as strong an effect on the falloff in gas generation as does matrix depletion. A pressure of 1000 kPa is generated in approximately 190 days of exposure for a 160X dose rate,[18] after which the rate of

pressurization is unaffected by any further pressure increases [see (6) below].[20] Finally, it apparently was not determined what effect, if any, the presence of oxygen might have on the magnitude of the increased rate of gas generation.

In the original presentation of the data on the synergistic enhancement of gas generation due to temperature, the percent increase in the rate of evolution was calculated in a cumulative manner in which each successive datum was averaged with all previous data.[16] In a later progress report, the same data were analyzed by a different approach.[18] Although not explicitly stated, this latter analysis apparently calculated the percent increase in evolution rate due to the 50°C temperature rise for each sampling period. This is a more accurate representation of the system's behavior since the later data are not biased by earlier trends or effects.

(6) Two types of experiment were conducted in order to determine the effect of pressure on gas generation rates. In experiments carried out at LASL, gases generated by radiolysis of cellulosics were allowed to accumulate and pressurize over the matrix (contaminated with $^{238}PuO_2$ to 160X). After 482 days, the test cylinder reached a pressure of approximately 1400 kPa.[20] This experiment was compared to a similar one in which the accumulated pressure was relieved at 95 to 100 kPa above ambient. This comparison showed that, in the case of self pressurization, the increase in pressure caused the rate of additional pressurization to slow, with the maximum difference between this rate and that for the pressure relieved experiment reached at 1000 kPa. After 1000 kPa, an increase in the self pressurized experiment did not continue to decrease the rate of pressurization (a comment will be made below concerning this observation).

These data are in agreement with results from Zerwekh.[14] Cylinders of Pu-238 contaminated cellulosics were allowed to self-pressurize to 690 kPa, sampled, depressurized, allowed to pressurize, etc. When compared to experiments in which the maximum pressurization allowed was 101 kPa, the rate of gas formation was less in the more highly pressurized cylinder. In addition, water formation from cellulosics was observed in cylinders that self pressurized to 690 kPa but not for the 101 kPa pressurization. A suggested explanation is the recombination of H_2 and O_2 at the higher pressures although this has not been experimentally proven. This is interesting in that the oxygen initially present is depleted in about 3 to 4 weeks,[17] and initial sampling of the high pressure cylinder occurred after 285 days of reaction. SRL results originally reported no change in the rate of pressurization up to 1380 kPa for the alpha radiolysis of concrete and TRU contaminated sludge simulant.[21] More recent data indicate still no change in the rate of radiolytic gas production in a concrete-TRU ash waste form allowed to self pressurize up to 3400 kPa.[12] This difference between LASL and SRL results can probably be attributed to the substrate that is undergoing radiolysis in each case.

In a second series of experiments, cylinders of cellulose and polyethylene contaminated with $^{238}PuO_2$ to a dose rate of 160X were pressurized with deuterium in order to generate information more rapidly. An isotope of hydrogen was used because hydrogen is one of the gases generated from alpha radiolysis of these matrices and because it is easily distinguished from any newly evolved hydrogen. For the cellulosics, three deuterium pressures were used: 3.4×10^3 kPa, 6.8×10^3 kPa, and 10.2×10^3 kPa. For polyethylene, only the highest deuterium pressure was used.

The polyethylene experiment was inconclusive due to a signficant leak in the test cylinder. The observed pressure increases for the cellulose experiments and for a comparison experiment are given in Table 4.4.[20] The data show that, as in the case of self pressurization, high gas pressures decrease the rate of gas generation from radiolysis of cellulose. This decreased rate of evolution has been attributed to the recombination of deuterium with the matrix accompanied by some hydrogen evolution to produce a net decrease in rate.[20] It can be seen from Table 4.4 that the rate of gas evolution continues to decrease until approximately 7×10^3 kPa. As noted in the discussion above concerning the self pressurization experiments, no additional decrease in the rate of gas pressurization was observed beyond 1000 kPa. The reason(s) for the different behavior in the self pressurization versus high pressure experiments has not been elucidated.[20]

Table 4.4

Effect of Pressure on Radiolytic Gas Generation
(This is Table I of Reference 20)

Experiment	Pressure (kPa)	Pressure Increase in 103 Days (kPa)
Comparison[a]	100	+658
Deuterium	3.4×10^3	+441
Deuterium	6.8×10^3	+227
Deuterium	10.2×10^3	+214

[a]Pressure is regularly relieved at 95-100 kPa above ambient.

4.3.2.2 Other Organic Waste Matrices (Polyethylene, Teflon, Neoprene, Hypalon, Pump Oil, Polyvinyl Chloride, Composite, and Bitumen)

This section will summarize the important results found for the above mentioned waste matrices.

(1) According to LASL results, low density polyethylene behaved in a similar manner to the cellulosics,[14] with some notable differences. The only major product from irradiation of thin (0.05 mm thick), low

density polyethylene was hydrogen. $G(H_2)$ decreased as a function of total dose.[14,17] After 1318 days, no gas generation (LASL) was observed from alpha radiolysis of 100% cross linked high density polyethylene (2.3 mm thick) contaminated with Pu-238 to about 50X.[14] In contrast to these results, a value of G(gas) (listed in Table 4.3; note this is not G°) of 0.73 (Pu loading of about 100X) was found at RFP for 0.08 mm thick polyethylene after 270 days of exposure.[17] A possible explanation for the discrepancy between LASL and RFP was given in Section 4.3.2.1. The only new information generated concerning alpha radiolysis of polyethylene during the period since the Interim Report was issued concerns G°(gas) values that were determined recently for a number of different waste matrices.[20] A G°(gas) range of 2.6-3.2 was estimated for polyethylene from an experiment in which the contamination level was 640 x 10^5 nCi/g (160X). Zerwekh[14] found a value of G°(gas) of 1.9 (dose rate approximately 50X) for polyethylene.

(2) A composite organic matrix consisting of 35% cellulose, 23% polyethylene, 12% polyvinyl chloride, 15% neoprene and 15% Hypalon (representative of typical LASL TRU waste) yielded mainly H_2 and CO_2.[14] Waste material typical of that from Mound Laboratory did not undergo degradation from alpha radiolysis after 400 days exposure.[14] This is quite surprising since the contaminant loadings and composition of the matrices were very similar in both experiments.

(3) Some confusing results have been reported for the radiolysis of polyvinyl chloride (PVC). In experiments conducted at LASL, PVC exposed to a dose rate of 1X had an induction period of 8 to 10 weeks.[16] G(gas, 70°C) was estimated to be 8 to 11 or greater, the largest G value observed for any matrix studied and the only one whose G(gas) increased with increasing total dose. Thermal degradation was ruled out by control experiments.[19] More recent results gave an estimated G°(gas, 70°C) of 1.0 for a dose rate of 160X.[19] It was stated that this "...value may be low if PVC requires an induction period..." It is not clear why the experiment of 1X dose rate, which reportedly has a considerable induction period, would yield a higher estimated G°(gas) range than the 160X dose rate experiment if the effect of the presence of oxygen is to yield G values that are too low. Some of the ambiguity in these results could have been alleviated if the experiments had been conducted under oxygen free conditions. The final G°(gas) range reported for PVC was 1-10.[20] The gases evolved from alpha radiolysis of PVC were composed mainly of hydrogen (90+ mol %), 4.5 mol % each of CO and CO_2, and a small amount of CH_4.[16] No chlorine species were detected by mass spectrometry although HCl has been reported to be a radiolysis product.[25,26]

In an additional report from LASL,[14] Pu-238 contaminated PVC (1X dose rate) produced only 10 cm^3 of gas after 335 days, leading the author to conclude that insignificant quantities of gas are generated by alpha radiolysis of this material. In alpha radiolysis experiments conducted at RFP, PVC was contaminated with Pu-238 (28X) and Pu-239 (4X).[21] A higher G(gas) was found in the case of the Pu-239, an anomalous result

in terms of dosage and matrix depletion. For other matrices, the G(gas) obtained by RFP was much lower than LASL's.

(4) Based on results for the radiolysis of pump or machine oil from LASL, SRL, and RFP, there is general agreement that hydrogen is the main product and that CO and CO_2 are produced at the expense of O_2.[14,17,21] The values for G(total gas) listed in Table 4.3 for pump oil are $G°(H_2)$ from SRL, G°(gas) from LASL, and G(gas) from RFP. The G values from SRL and RFP have been corrected for energy absorption by the chemical absorbent used in these experiments. The contaminant loading was about 280X for SRL, the lower limit for RFP was about 4X. In the case of the LASL experiments, the production of gas for a contaminant loading of 25X was approximately the same as that for a loading of 50X. Regardless of the differences in experimental conditions among the various laboratories, $G(H_2)$ is significant for hydrocarbon oil as substrate.

(5) Bitumen immobilization of radioactive waste is used extensively in the Federal Republic of Germany by the Eurochemic Facility in Belgium, and by the Japan Atomic Energy Research Institute. Both high dose rate (160X) and low dose rate (1X) experiments were conducted at 20° and 70°C.[18,27] As for cellulosics, G(gas) decreased with increasing dose presumably due to matrix depletion. A G°(gas) of 1.4 was estimated from the high and low dose rate experiments.[27] Within the experimental precision of 30% observed in the LASL data, it was concluded that the rate of gas generation from bitumen was unaffected by a 50° increase in temperature. A temperature dependence has been obtained for radiolysis of cellulose and no explanation was offered for the difference in behavior for these two materials.[18] It would seem apparent that the mechanisms of radiolytic degradation are not identical and that one or more steps in the mechanisms for cellulose degradation may be temperature dependent. Gases generated from bitumen included H_2 (97 mol %), CH_4 (2 mol %), and CO_x (1 mol %), with traces of higher molecular weight hydrocarbons.[18,27] No significant compositional changes occurred with increasing dose. The implication of these results was that enough hydrogen was generated from alpha radiolysis to be of concern, from a safety viewpoint, in the handling, transportation, and storage of bitumen encapsulated TRU waste.

(6) G°(gas) values were reported for the alpha radiolysis of Teflon (0.08),[20] Hypalon (0.2), and Neoprene (0.05).[19,20] The value for Hypalon is notably higher than that reported elsewhere (no gas generation after six months irradiation at a dose rate of approximately 50X).[14]

4.3.2.3 Concrete

Waste acceptance criteria extend beyond organic combustible wastes to other potential gas producers that might be placed in a repository. One waste form that has potential as a candidate material for solidification of TRU contaminated incinerator ash and process sludges is concrete. Experimental studies of gas evolution from the alpha radiolysis of concrete have been conducted at SRL.

The objectives of the SRL program are to determine (a) the relative gas generation capacities of concretes versus organic matrices, and (b) techniques and additives that could significantly reduce the gas generation rates of concrete.

In the studies on process sludge incorporation, samples of simulated Savannah River Plant wastes were mixed with a high alumina cement to make concretes.[28] The cement composition used was (by wt. %) Al_2O_3, 41; CaO, 37; SiO_2, 9; Fe_2O_3, 6; and MgO, 2, plus some other oxides. Alpha radiolysis experiments were performed with concrete containing 40% (w/w, dry) SRP simulated wastes plus a known amount of Cm-244. The simulated waste was composed of equimolar mixtures of Fe(III) and Al(III) hydroxides or of Fe(III) and Mn(IV) hydroxides. The significant results for the alpha radiolysis of concrete containing simulated SRP sludge are:

(1) Both oxygen and hydrogen were produced in a O_2/H_2 ratio that varied from 0.2 to 0.5.

(2) For a dose rate of 2.8×10^{20} eV/hr (about 75X), the total gas pressure increased nearly linearly up to the maximum tested pressure of 1380 kPa. For gamma radiolysis under similar experimental conditions, a maximum steady state pressure of about 345 kPa is attained.[28]

(3) The G values reported were $G(H_2) = 0.21$ and $G(O_2) = 0.10$. $G(H_2)$ appeared to be independent of dose rate over the range studied (1.6 to 2.8×10^{20} eV/hr).

(4) An estimate of the long term pressurization of a sealed canister, typically 2 feet (I.D.) x 10 feet tall (10% free volume), containing concrete plus SRP wastes was made. The conceptual waste composition included Sr-90, Cs-137, Pu-238, and Pu-239. For the waste container and other assumed conditions (e.g., volume, weight of waste, dose, etc.), a final pressure of 2100 psig (14.5 MPa) after 10^5 years was calculated.

The evolution of gas from alpha radiolysis of concrete containing simulated and actual TRU incinerator ash has been investigated at SRL. The concrete-TRU ash formulations were prepared from high alumina cement (HAC), Portland Type-I cement (I), and Portland-Pozzolanic cement (I-P). The compositions of these cements are given in Table 4.5. For the case of simulated ash, concrete samples were prepared by mixing 30% (dry weight) ash in the dry cement mix with a Pu-238 solution or by adding PuO_2 particles to the mix. Concrete samples made with actual incinerator ash were prepared by mixing the dry cement with approximately three grams of contaminated ash plus enough noncontaminated ash to bring the total ash content to 30% (dry weight). The cement paste was allowed to cure either in plastic molds after which they were placed in steel cylinders equipped with pressure transducers or the paste was poured directly into steel cylinders and allowed to cure. In general, the concrete was cured at ambient conditions during which time 30 to 40% of the free water evaporated. The simulated ash was obtained from incineration and calcination (at 800°C) of typical SRL TRU laboratory wastes. The composition of this simulated ash is given in Table 4.6.

Actual contaminated ash was prepared by incinerating laboratory waste contaminated with a Pu-238 solution. The exact composition of this ash was not determined. The G values for these experiments were calculated from the rate of pressure change and also from the final gas composition and total dose. If oxygen is depleted by radiolysis, the G(gas) value calculated from the rate of pressurization will be less than that calculated for $G(H_2)$ from the final composition. The results obtained for the alpha radiolysis of concretes are summarized in Tables 4.7 and 4.8 and discussed below.

Table 4.5

Composition of Various Cements
(This is Table 1 of Reference 29)

Cement Type	Composition, wt %						
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3[a]	Other
High Alumina	36.5	8.5	40.5	5.5	1.0	0.2	7.8
Portland Type-I	63.1	21.3	5.8	2.6	2.9	1.8	2.5
Portland-Pozzolanic	50.5	37.0	4.7	2.1	2.3	1.5	1.9

[a] Present as sulfate.

Table 4.6

Noncombustible Content of Calcined Simulated TRU Incinerator Ash (mole %)[a]
(This is Table 2 of Reference 29)

Calcium	42	Boron	0.3	Chromium	0.04
Titanium	41	Chlorine	0.2	Fluorine	0.02
Silicon	6	Sodium	0.2	Antimony	0.02
Aluminum	5	Sulfur	0.07	Manganese	0.02
Magnesium	3	Strontium	0.06	Molybdenum	0.006
Phosphorus	0.6	Zinc	0.05	Copper	0.003
Barium	0.4	Nickel	0.04	Vanadium	0.003

[a]Results calculated excluding C, N, and O which could not be detected by spark source mass spectrometry. Results accurate within a factor of two.

Table 4.7

Radiolysis Data of High Alumina Concrete-TRU Ash Samples
(Some of these data were obtained from Table 4a of Reference 11)

Test Condition	T°C (±2°C)	G(H_2)	G(Total Gas)
Individually Cast (5.0 cm x 1.7 cm O.D.), Removable Mold			
Without ash, Pu(L), hdr	23	0.42	0.33
With ash, Pu(L), hdr	23	0.55	0.51
With ash, Pu(L), mdr	23	0.48	0.24
With ash, Pu(L), ldr	23	0.47	-0.29
With ash, Pu(L), hdr	70 sh	0.24	0.14
	70 hs	0.15	0.17
	23[a]	0.13	0.15
With ash, Pu(S) hdr			
Non-heated (28% water)	23	0.21±0.01	0.21±0.03
Heated at 200° (17% water)	23	$0.02\overline{2}$	$0.01\overline{6}$
With ash, EDTA,[b] Pu(L), hdr	23	0.30	0.15
	70 sh	0.19	---
	70 hs	0.060	0.040
With ash, 0.01 M $Fe(NO_3)_3$, Pu(L)	23	0.30	0.25
With ash, 0.10 M $Fe(NO_3)_3$, Pu(L)	23	0.18	0.22
With ash, 1 M $Fe(NO_3)_3$, Pu(L)	23	0.080	0.43
With ash, 2 M $Fe(NO_3)_3$, Pu(L)	23	0.030	0.43
With ash, 0.3 M $NaNO_2$, Pu(S)	23	0.15	0.14
With ash, 1 M $NaNO_2$, Pu(S)	23	0.079	0.087
With ash, 3 M $NaNO_2$, Pu(S)			
Non-heated (36% water)	23	0.084	0.030
Heated at 200° (27% water)	23	0.031	0.023
With ash, 5 M $NaNO_2$, Pu(S)	23	0.053	0.025
Cast in Steel Canister (10 cm x 2.3 cm I.D.)			
With ash, Pu(S), hdr	23	0.28±0.04	0.31±0.01
Non-simulated ash, hdr	23	$0.29\overline{}$	$0.30\overline{}$
Heated at 90°C (23% water)	23	0.15	0.13
Heated at 200° (14% water)	23	0.00070	-0.011

Notes: Pu(L) = Pu-238 in 0.2 M H_2SO_4
Pu(S) = particulate $^{238}PuO_2$
hdr = high dose rate, 10^{17} eV/min/g
mdr = medium dose rate, 10^{16} eV/min/g
ldr = low dose rate, 4 x 10^{15} eV/min/g
sh = sealed, then heated
hs = heated, then sealed

[a]Sample heated to 100°C, then sealed; experiment performed at 23°.
[b]Ethylenediaminetetraacetic acid.

Table 4.8

Radiolysis Data of Portland Type-I Concrete-TRU Ash Samples
(Some of these data were obtained from Table 4b of Reference 11)

Test Condition	T°C (±2°C)	$G(H_2)$	G(Total Gas)
Individually Cast (5.0 cm x 1.7 cm O.D.), Removable Mold			
Without ash, Pu(L), hdr	23	0.43	0.48
With ash, Pu(L), hdr	23	0.65	0.55
With ash, Pu(L), mdr	23	0.63	0.61
With ash, Pu(L), ldr	23	0.66	0.23
With ash, Pu(S), hdr	23	0.28	0.27
With ash, Pu(L), hdr	70 sh	0.48	0.46
	70 hs	0.15	0.17
	100 hs	0.11	0.050
With ash, EDTA, Pu(L), hdr	23	0.35	0.050
	70 sh	0.31	0.29
	70 hs	0.084	0.067
	100 hs	0.054	0.025
With ash, 0.01 M $Fe(NO_3)_3$, Pu(L)	23	0.34	0.31
With ash, 1 M $Fe(NO_3)_3$, Pu(L)	23	0.080	0.43
With ash, 2 M $Fe(NO_3)_3$, Pu(L)	23	0.030	0.16
Cast in Steel Canister (10 cm x 2.3 cm I.D.)			
With ash, Pu(S), hdr			
Non-heated (30% water)	23	0.32	0.49
Heated at 90° (28% water)	23	0.20	0.30
Heated at 100° (8.2% water)	23	0.0090	0.010
Heated at 200° (7.5% water)	23	0.00030	-0.017

(1) The oxygen content of the gas mixture evolved from alpha radiolysis of several concrete-TRU ash samples has been found to be variable. However, the factor(s) affecting the variability is not clear. In the case of some concrete-TRU ash formulations, the concrete paste was allowed to cure in removable plastic molds.[24,29,30] In no case where plastic molds were used was oxygen produced. One explanation given for this behavior is the possible reaction of oxygen precursors with something that might have leached from the plastic molds.[11] If the concrete was cast and cured in steel cylinders, oxygen was produced,[21,30,31] except for the case where the concrete samples (both HAC and I) were made with actual incinerator ash.[31] Bibler stated that the form of the plutonium, as solid $^{238}PuO_2$ or ^{238}Pu-contaminated incinerator ash, made no difference as far as any affect on $G(H_2)$.[31] The data substantiate this claim; however, such is not the case concerning $G(O_2)$. If the form of the plutonium is unim-

portant, then why the difference in oxygen behavior for samples that do not involve plastic molds? Certainly, a useful experiment would be to prepare a concrete sample using the simulated ash and Pu-238 in solution.

Two experiments were performed to determine if iron (from the steel cylinder surface) could be producing oxygen by reducing the radiolytically generated H_2O_2.[31] The experiments showed that the presence of iron did not cause oxygen production. Adding to the confusion concerning oxygen behavior is the fact that, for two Portland Type-I concrete-TRU ash samples both prepared from simulated ash doped with $^{238}PuO_2$ and cured in steel cylinders, a ratio of $G(O_2)/G(H_2)$ of 0.38 was found in one case[21,31] and 0.54 to 0.57 in the other.[30] The smaller ratio indicates that less than a stoichiometric amount of oxygen was formed, probably due to generation of another oxidation product of water, such as H_2O_2. Again the question arises: Why the difference in behavior between these apparently similar systems? At this time the following statements can be made concerning the behavior of oxygen in concrete-TRU ash systems under alpha radiolysis conditions:

(a) Clearly, curing of the concrete samples in plastic molds results in either a decrease in oxygen content or no change at all. A possible explanation for this behavior was given above.

(b) The effect on oxygen content of doping the concrete with particulate PuO_2 versus plutonium in solution is not clear.

(c) What effect, if any, the ash has on the behavior of oxygen is not known, as discussed above. Furthermore, it should be noted that simulated ash resulted from incineration and calcination. The actual contaminated ash apparently was not calcined. There may be an important difference in the chemical composition of these ashes that affects the mechanism of oxygen production or depletion under radiolytic conditions.

(d) Other factors, such as curing time, may be important in these systems.

(e) A system such as concrete-TRU ash under radiolytic conditions is complicated. Bibler has noted that, although oxygen is a product from the alpha radiolysis of liquid water, the mechanism for its formation has not been clearly established.[31] The presence of cement powder and incinerator ash only serves to complicate matters. It is well known that the behavior of reactions involving free radical intermediates is quite sensitive to experimental conditions.[32] In addition, the progress of such reactions is normally impeded by the presence of dissolved oxygen. Some of Bibler's data are indicative of such behavior (e.g. see Figure 5 of Reference 24).

(f) Finally, the formation of oxygen serves to increase the total pressure in a sealed container of concrete-TRU ash and in the presence of the hydrogen generated, presents a potentially hazardous situation.

(2) For ash free samples of HAC, I, and I-P contaminated concrete cast in plastic molds, hydrogen was the only gas produced, and in some cases, oxygen was depleted.[29] The depletion of O_2 accounts for the fact that $G(gas) < G(H_2)$. $G(H_2)$ increased in the presence of added ash due to its water content. Since no difference in results was observed between I and I-P concretes, the latter was eliminated from further study. Control experiments conducted with nonradioactive samples of HAC and ash at three different temperatures confirmed that both hydrogen production and pressurization resulted from radiolysis.[24]

(3) $G(H_2)$ for both HAC and I concrete-TRU ash samples was found to be independent of temperature up to 100°C.[24] The reason for this is felt to be the probability that no competing processes exist that scavenge H_2 precursors. $G(H_2)$ for both HAC and I concrete-TRU ash samples was also found to be independent of dose rate over the range 4×10^{15} to 1×10^{17} eV/min/g (which corresponds to 3.5×10^{-4} to 8.8×10^{-3} Ci/g of concrete).[29,30]

(4) $G(H_2)$ was determined to be independent of the pH (0.6 to 7) of the water used in mixing the cement and ash.[29] Previous experiments had used Pu-238 dissolved in 0.2 M H_2SO_4 solution. Actual waste will be added to the cement as a solid and the concrete will be made with neutral water. Thus, it was important to determine the pH dependence of $G(H_2)$.

(5) When Pu-238 was added as solid PuO_2 particles rather than being dissolved in the water used to make concrete, the G(gas) dropped from 0.51 (Pu, L) to 0.21 (Pu, S) for HAC and from 0.55 (Pu, L) to 0.27 (Pu, S) for Type-I concrete.[24] The decrease in G is due to the absorption of some of the alpha energy by the larger PuO_2 particles. However, as noted in (1) above, no significant difference was observed for $G(H_2)$ whether the plutonium was added as PuO_2 or Pu-238 contaminated ash from incineration of combustibles contaminated with dissolved plutonium. $G(H_2)$ for HAC containing actual Pu-238 ash was 0.29 as compared to 0.25 for HAC containing ash doped with $^{238}PuO_2$.[31] The implication is that concrete containing Pu-238 ash can be considered a sample of actual TRU waste ash immobilized in concrete rather than a sample containing simulated ash.

(6) In the beta-radiolysis of concrete, $G(H_2)$ decreases with increasing hydrogen pressure and, eventually, an equilibrium pressure is reached.[28] As part of that same study, no effect of hydrogen pressurization up to 1380 kPa was observed under alpha radiolytic conditions. Other high pressure tests conducted at SRL have recently been reported.[30] After some 800 hours irradiation time, a PuO_2 doped sample of Portland Type-I concrete-TRU ash has developed a total pressure of 1380 kPa and the pressure is continuing to increase nearly

linearly with time. This experiment was terminated after 2000 hours and a total pressure of 3450 kPa had accumulated.* Still, no pressure effect was observed.

(7) G(gas) values were significantly decreased by addition of scavenging agents such as nitrate and nitrite ions that reacted with H atoms and solvated electrons (hydrogen precursors). Addition of NO_3^- (as ferric nitrate) decreased $G(H_2)$ from 0.55 to 0.030 (2 M NO_3^-) for HAC and from 0.65 to 0.030 (2 M NO_3^-) for Portland Type-I cement.[31] However, oxygen production was significant. This results from radiolytic reduction of nitrate ions.[32] Nitrite ions were added to cement/ash mixes in which PuO_2 particles had been incorporated. Acid solution could not be used because of the instability of nitrite ions at low pH. For 5 M $NaNO_2$, $G(H_2)$ was reduced from 0.22 to 0.053.[31] Also, oxygen was consumed in the presence of NO_2^-, indicating oxidation of NO_2^- to NO_3^-. Since oxygen is consumed in the presence of added nitrite ions, addition of NO_2^- to reduce hydrogen production would be better than addition of nitrate ions. The relative decrease in $G(H_2)$ upon addition of NO_3^- or NO_2^- is shown in Figure 4.2. (The data plotted in this Figure are from tables listed in Reference 31. It would appear that the data in Figure 2 of Reference 31 are incorrectly plotted.) The data for NO_3^- follow the trend for the effect of NO_3^- in the alpha radiolysis of liquid water as shown by the solid line. This similarity suggests that these ions are probably reacting as they do in liquid water. This is evidence, along with $G(H_2)$ being independent of temperature (between 22 and 100°C) and dose rate, that the radiolytic reduction of H_2O in concrete is similar to the radiolytic reduction of liquid H_2O. From Figure 4.2, it appears that NO_2^- ions are less effective than NO_3^- ions.

(8) Another approach used to reduce gas yields was lowering the water content by heating the concrete to remove free water. Most of the water in concrete was removed by heating (200°C) for several hours. This reportedly does not severely affect the strength of the concrete.[33] As can be seen from the results in Tables 4.7 and 4.8, $G(H_2)$ was greatly reduced for HAC and Type-I concrete.[31] Heating had little effect on $G(H_2)$ for an HAC sample that contained NO_2^-.[31] The tremendous decrease in gas yields due to removal of free water indicates that the water involved in the hydration reactions is not very susceptible to radiolysis, possibly because of the ability of the water of hydration to transfer absorbed energy without undergoing decomposition.

(9) Specially prepared concretes that have a low water content are being investigated as potential TRU waste forms. These were discussed in greater detail in Section 2.5. One such formulation that has been developed for the transuranic waste generated at Mound Facility (MF) is

*N. E. Bibler, Savannah River Laboratory, private communication to G. Bida, BNL, March 23, 1981.

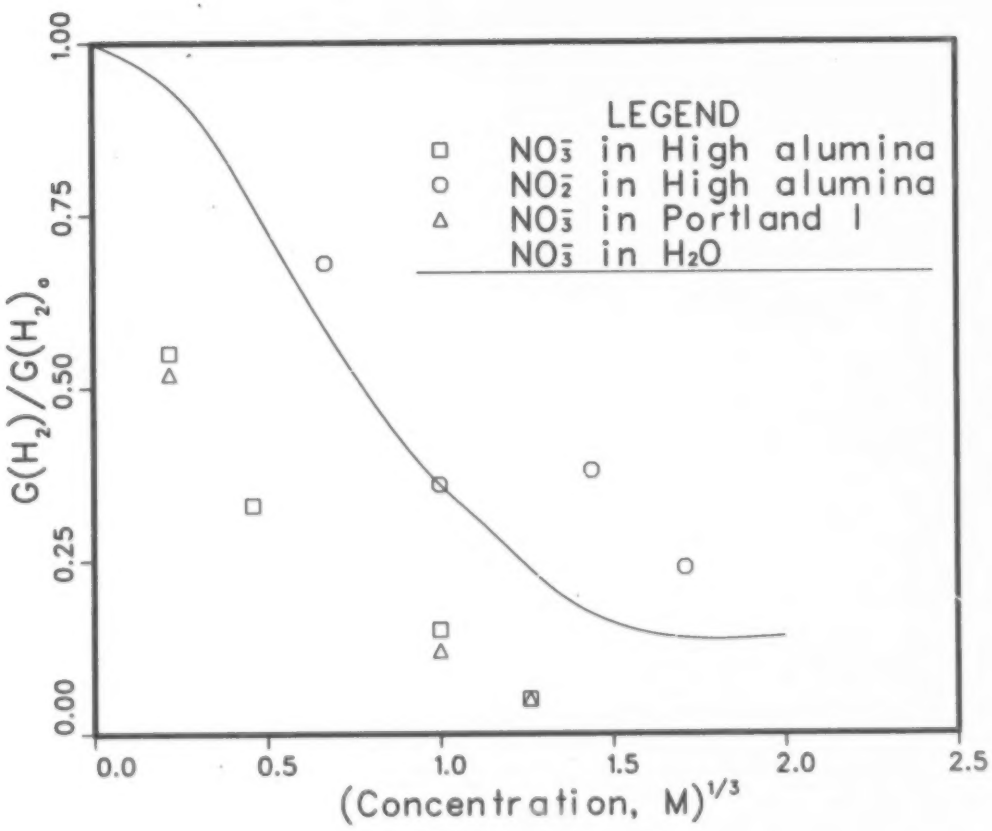

Figure 4.2 Fractional lowering of $G(H_2)$ by adding NO_2^- or NO_3^- to concrete.

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Cementitious Pelletized Waste Form (CPWF) concrete. This concrete is prepared by pressing the cement-ash paste at 173 MPa at room temperature and then allowing it to cure. SRL has investigated the gas production from this concrete. The following samples were prepared, all containing 65 weight % (dry basis) simulated ash: (a) pressed concrete-ash prepared at SRL, (b) pressed concrete-ash prepared at MF from their own ash simulation, and (c) pressed concrete containing bone char ash (an adsorbent for plutonium). Results of the radiolysis experiments conducted at SRL for Portland Type-I cement containing the three different simulated waste compositions are summarized in Table 4.9.[31] The two higher $G(H_2)$ values reported for the MF ash and bone char were for samples that had sorbed about 2.3 weight % water upon standing at ambient conditions. Mound conducted radiolysis experiments for their own cement-ash pellets (same composition as above) and reported an average $G(H_2)$ of 0.013.[34]

Table 4.9

Pressed Concrete Pellet Results

Simulated Waste	$G(H_2)$
SRL Ash (primarily Ca, Ti)	0.0050
MF Ash (primarily Si, Ca)	0.0090-0.015
Bone Char (primarily Ca, C)	0.0030-0.0046
Pellet Weight Composition: 65% ash (dry), 35% Portland Type-I cement (dry), 3% water.	

Another specially prepared concrete that has been examined for rate of gas generation from alpha radiolysis is FUETAP (see Section 2.5.2). A sample of this material was doped with Cm-244 and prepared under standard curing conditions (normally a 1.5 h heatup period followed by a 22.5 h curing at 250°C and 4.1 MPa). The sample was then dewatered at 250°C. After approximately 150 days irradiation, a gas production rate of 3.0 to 3.5 cm^3/year (STP) was reported for a sample having a Cm-244 concentration of 0.4 mg/g of concrete (which is about 3×10^7 nCi/g).[35] For comparison, the production rate from a concrete specimen cured under ambient conditions was 58 cm^3/year (STP) and was decreasing with time. We have estimated a G(gas) value from these data by assuming that the sample is a right circular cylinder of dimensions 1.3 cm diameter x 3 cm long and has a density of 2.0 g/cm^3.[35] It was further assumed that G(gas) is independent of dose and dose rate. For these assumptions, the estimated G(gas) is 0.005. This value is comparable to that found for the SRL and MF cold pressed concretes. In the case of FUETAP, the low gas production is probably due to a combination of low water content and the reported catalytic activity of FUETAP that results in the recombination of radiolytically produced hydrogen and oxygen.[36]

(9) Rewetting both the pressed concrete and the dehydrated (200°C) samples resulted in significant increases in $G(H_2)$.[31] This emphasizes the importance of maintaining a water free environment in the case of these waste forms.

The rate of hydrogen gas generation from TRU ash incorporation has been calculated for an assumed scenario:[24] (a) the concrete-TRU ash was contained in a 210-liter drum with a 10% void volume plus an assumed 10% porosity for the concrete; (b) the concrete contained 200 grams of Pu-239; (c) $G(H_2)$ was assumed to be independent of pressure and dose; (d) all the alpha decay energy was absorbed by the waste form, and (e) the 210-liter drums are leak tight. The pressure increase as a function of storage time for various waste treatments or additives is shown in Figure 4.3.[31] The porosity of a concrete-ash sample has recently been determined to be 15% of the concrete volume.[30] This change in porosity means an 18% lower pressure in the drums for the same radiation dose than for the assumed porosity of 10%. The consequence of the container pressurization, e.g. in terms of handling, storage, etc., was not discussed.

4.3.2.4 Field Studies

Some important data have been collected at LASL,[14] SRL, and RFP on gas generation in drums of production wastes.[11] The experiments were conducted on drums either in the field, brought back to the laboratory, or under field conditions simulated in the laboratory. At LASL, 115 liter drums of Pu-238 contaminated or 210 liter drums of Pu-239 contaminated organic wastes were periodically monitored for their gaseous content and, in the case of Pu-238, temperature and pressure. The amount of contaminant in the drums ranged from about 3×10^3 to 3×10^5 nCi/g of waste for Pu-239 and approximately 10^7 nCi/g for Pu-238. In addition to these experiments, gas mixtures from some of the drums contaminated with Pu-238 and from the cylinders containing hydrogenous wastes were evaluated for their explosive potential. The results from these and other tests are as follows:

(1) No significant pressurization above one atmosphere was observed in any of the drums due to gaseous diffusion through the drum sealing gaskets.

(2) Little evidence for gas generation from Pu-239 alpha radiolysis was seen, due mainly to the low rate of gas generation coupled with diffusion of gas into and out of the drums. This does not imply that an explosive mixture is not possible in these waste containers, especially if the sealing were improved.

(3) Drums containing Pu-238 contaminated wastes generated gases, most notably H_2. Again, amounts could not be determined because of diffusion. Some of the gas mixtures in the drums were found to be explosive.* After a period of time, some of the mixtures reached

*Hydrogen is commonly accepted to be explosible in air when present in the 4-76% (v/v) range.

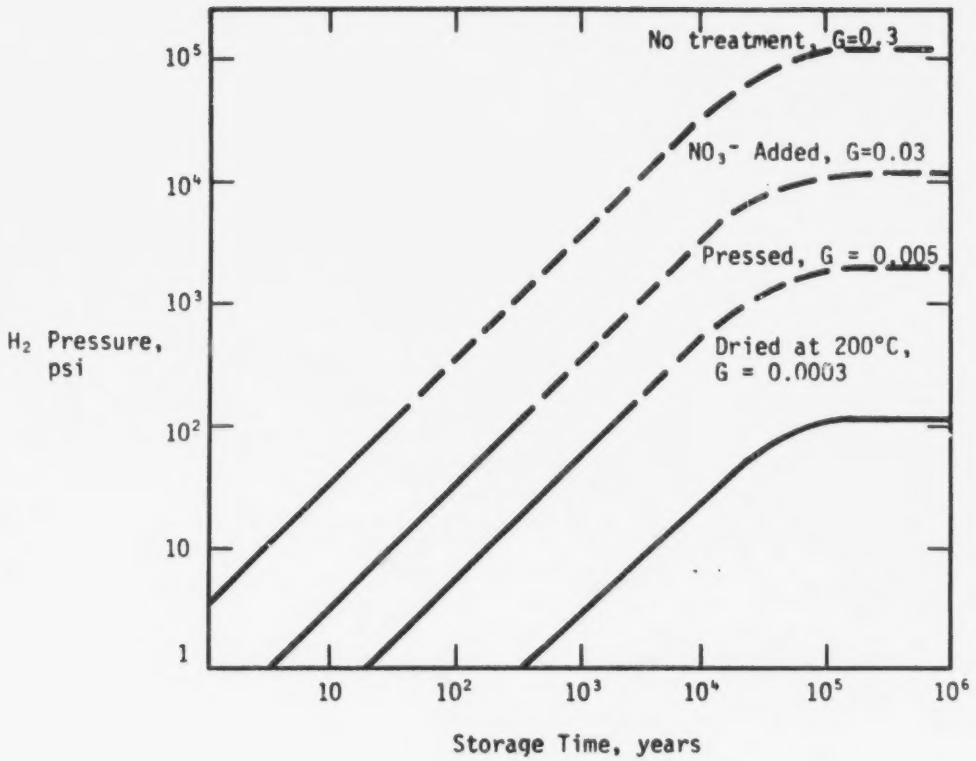

Figure 4.3 Calculated long term radiolytic H_2 pressure in a 210-L drum 90% full of Portland concrete containing 200 g of Pu-239.
(This is Figure 13 of Reference 31.)

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combustible compositions. Hydrogen concentrations increased with time and the oxygen was depleted due to CO and CO_2 formation. According to Zerwekh,[14] because of air diffusion into any storage drum, all drums of Pu-238 contaminated hydrogenous waste in interim storage must be considered potentially explosive until their gaseous contents have been analyzed and/or replaced with inert gas.

(4) Due to the mixture of gases typically found in TRU contaminated waste containers (H_2, CO, CO_2, CH_4, residual air, and trace hydrocarbons), it is suspected that it might have different explosive limits than for hydrogen in air. Experiments conducted to establish the explosive limits of gas mixtures from radiolytic degradation of the organic wastes indicated that mixtures with $H_2 < 6$ mol % are probably not explosive. Pu contaminated wastes buried (5 years) in culverts at SRL resulted in hydrogen concentrations that exceeded minimum explosive limits.[14]

(5) Similar results were obtained for drums containing typical SRP wastes.[37] Hydrogen concentrations as high as 25% (v/v) were detected.

4.3.2.5 Contaminated Soils

Gas generation from radiolysis of TRU contaminated soils is included here for completeness. The results discussed in this section were obtained from reports relating to plutonium mining operations conducted at the Hanford site.

It is estimated that some 14 million m^3 of transuranic contaminated soil exist at various DOE locations. What fraction, if any, of that soil will have to be processed into an immobilized waste form has yet to be determined. Methods for processing contaminated soil have been discussed in Section 2.4 and elsewhere.[38] Contaminated soil is not anticipated to be a major component of TRU waste from commercial reprocessing. However, it is not clear if this waste stream complies with proposed regulatory guidelines[3] for a licensed repository. Section 60.133(b)(2) of 10 CFR 60 on stabilization may preclude disposal of contaminated soil without immobilization. This section on the gas generation from alpha radiolysis of contaminated soils is intended to provide additional information for consideration in the development of regulations pertaining to the allowability of this material in a repository.

From 1955 to 1962, an enclosed earthen trench, designated 216-Z-9 and sometimes referred to as the Z-9 "crib," was used for the disposal of both organic and aqueous plutonium waste solutions from the Recuplex Plutonium Scrap Recovery Facility located at the Hanford Reservation.[39] For reasons related to nuclear criticality considerations, a cadmium nitrate solution was sprayed on the soil contained in the Z-9 crib. Sometime thereafter it was decided to remove the top 30 cm of contaminated soil as a means of reducing the risk of environmental contamination. These measures were also intended to conform with the criterion requiring solid TRU wastes to be packaged and retrievably stored for 20 years.[40] Z-9 mining operations began in earnest in early 1977 and lasted for about 18 months. Soil samples were poured into 10-L canisters which were then

sealed. These were placed into 0.3-mm polyethylene bags and then canisters plus bags were placed into a second, larger outer canister. After assaying for plutonium content, the canisters were loaded into 210-L drums. The drums normally accommodated eight canisters of soil. It was reported that 5,222 canisters containing a total of 58 kg of plutonium were filled over the 18-month mining period.

Prior to the initiation of mining operations, radiolytic decomposition of organics and water was recognized as being the source of a potentially explosive mixture of hydrogen and oxygen. Using data available at that time, the time required for the gas in a drum to reach the explosive limit of hydrogen in air was estimated to be three months, and as little as two days for drums containing the maximum allowable plutonium content.[39] A program was established to experimentally determine gas evolution rates from Z-9 soil samples as a function of the plutonium, moisture, and organic content of the soil.[41] The findings of this program are summarized below.

(1) Eight soil samples were taken from canisters chosen to represent a range of soil compositions. Soil sample analyses gave the following ranges of properties:

   (a) The moisture content ranged from 6.2 to 30% (w/w). Water was intentionally added to two samples to increase the moisture content to 30 weight % in an attempt to establish the maximum gas generation rate. A moisture content between 0.2 and 24 weight % was reported elsewhere.[39]

   (b) The organic content was found to be 1.5 to 19% (w/w). Other sources reported a range of 0.2 to 46% (W/W), averaging 7.1% (w/w).[39] The organic content was, on average, slightly higher than the moisture content.

   (c) The plutonium content for the soil samples was determined to be 1.6×10^5 to 1.0×10^6 nCi/g.

(2) The two samples with 30 weight % water content showed an anomalous behavior in terms of gas generation rate and were excluded from consideration in interpreting the results.

(3) Gas evolution rates for each soil sample were determined for the gas mixture and for each gas component. The rates were found to increase with an increase in the combined organic and water content. The maximum gas production rate measured was 3.2×10^{-5} mole/d/g Pu. From another set of data for which the evolution rate was 2.4×10^{-5} mole/d/g Pu, we estimate a minimum G°(gas) of 6.0. When compared to G°(gas) values for the radiolytic degradation of organic matrices listed in Table 4.3, it is seen that contaminated soils potentially have the largest gas evolution rates under radiolytic conditions. It must be kept in mind, however, that, as for the other contaminated matrices, the amount of gas evolved will strongly depend on the contamination level in the soil and the organic/moisture content.

(4) The composition of a gas mixture evolved from a water rich soil sample was analyzed by mass spectrometry. It was noted that a significantly different composition could be generated from organic rich soil; however, no data were presented to substantiate this claim. The gases generated were mainly N_2 (49.5 mol %), O_2 (14.1 mol %), H_2 (23.3 mol %), and CO_2 (13.1 mol %). Similar to the radiolysis of cellulose (see Section 4.3.2.1), the initial presence of oxygen (soil samples were air equilibrated prior to the experiments) may have yielded an actual rate of O_2 production that is less than what would be found if the experiments were conducted under an inert atmosphere. We suggest this possibility because it is quite likely that oxygen is being generated and depleted at the same time. In the absence of added nitrate, oxygen has been found to be depleted,[28] generated,[42], or remain unchanged[29] for the alpha radiolysis of various concrete waste forms for TRU waste immobilization under different experimental conditions. For the experiments involving contaminated soil, a possible source of oxygen is the alpha radiolysis of nitrate ions. This has been studied in detail elsewhere.[29] In contrast to the generation of oxygen, Pajunen[41] reported that most of the soil samples displayed an initial time period during which no gas was generated and for which he offered no explanation. Oxygen inhibition of reactions involving organic radical intermediates is a well known phenomenon.[43] After the oxygen or the organic substrate is consumed, the reaction will commence. The lengths of the induction periods observed in these experiments did not correlate well with the reported organic content but rather they seemed to decrease with increasing plutonium content. The length of the induction period depends on several factors, including the amount of dissolved oxygen present. The observations detailed for gas generation from the water rich (30 weight %) soil sample are consistent with the oxygen inhibition hypothesis: no induction period was observed since the soil was either water rich (i.e. low in organics), or, due to a lack of records, the radiolysis may have been performed with a sample that was used to determine the moisture and organic content. In any case. the rate of change in oxygen content can be complicated and quite sensitive to experimental conditions. If for no other reason, these experiments should have been done under O_2 free conditions since, possibly fortuitously, the reported N_2/O_2 ratio for soil radiolysis is the same as that for air. This seems odd since the rate of nitrogen production was found to be at least three times greater than that for oxygen.

(5) It is obvious from the gas analysis that explosive hydrogen/oxygen mixtures are generated by radiolysis of Pu contaminated soils. For this reason, the Z-9 mining operation initiated a program in which the 210-L drums containing the soil canisters were retrofitted with gas vents and/or a catalyst that allowed for recombination of the hydrogen and oxygen. It should be noted that, due to the large ratio of organic to water content and the higher H_2/O_2 ratio in organics, the catalyst will allow recombination of hydrogen and oxygen until the oxygen is depleted. However, hydrogen will still be produced and should be viewed as a potentially hazardous situation in terms of a drum breach scenario involving personnel.

4.3.3 Thermal Gas Generation

The thermal degradation of waste matrices such as paper, cotton, composite and polyethylene at temperatures of 20°, 40°, 70°, and 100°C has been studied at LASL. The thermal degradation studies consisted of two phases: (1) determination of threshold decomposition temperatures for a broad range of common laboratory materials and (2) surveillance experiments on selected waste matrices. Thermal degradation was monitored via thermogravimetric analysis to determine threshold decomposition temperatures and gas generation rates. The following observations concerning thermal degradation of organic matrices have been made:

(1) Materials such as rags, paper, polyethylene, PVC, latex, butasol and neosol did not decompose in air up to 150°C. At 200°C, all test specimens began to char and decompose. Thermal decomposition temperatures in air ranged from 175°C to 205°C for cellulosics, 150°C to 210°C for plastics, and 165°C to 195°C for rubber materials. Asphalt began to decompose at 275°C.[16,44]

(2) Some studies were conducted under anaerobic conditions since oxygen was shown to be consumed in previous experiments.[16] Threshold decomposition temperatures under anaerobic conditions did not vary significantly from those found in air. It was determined elsewhere[45] that the thermal degradation mechanism for cellulose was nonoxidative. Thus, the threshold decomposition temperatures under aerobic and anaerobic conditions should be about equal.

(3) The potential effects on decomposition temperature of catalysts found or formed by storing drums of TRU waste in a salt repository were investigated. Catalysts included NaCl, Fe_2O_3, $FeCl_2$, and Fe powder (2 to 38% w/w loading). These catalysts showed only minor changes in threshold temperatures ($\pm$ 30°C from no catalyst situation).

(4) Kosiewicz noted that although the observed threshold decomposition temperatures are significantly higher than the maximum anticipated repository temperatures, the organic matrices might still slowly decompose over long time periods and accumulate appreciable quantities of gas.[44] Gas analyses have shown that cellulose does undergo thermal degradation at 100° and 70°C,[16,18,44] and possibly at 40°C. Apparently this is the first time that thermal degradation of cellulose has been demonstrated to occur at temperatures as low as 100°C. Two other organic matrices, polyethylene and a composite, underwent degradation at 100° and 70°C.[44] Because the gas generation rates for these experiments are so low, significant uncertainties exist in these data. These uncertainties are due to oxygen depletion (a factor that has been discussed in Section 4.3.2.1) and the possibility that gas generation due to bacterial degradation is occurring simultaneously, thereby masking trends from thermal degradation.[16] Gas generation due to microbial degradation will be discussed in Section 4.3.4. In partial

support of this hypothesis, the gas generation rate measured at 70°C (LASL) for cellulose is about five orders of magnitude greater than the predicted rate,[46] indicating that some other degradation mechanism may be operative. It was concluded from these data that gas generation due to thermal degradation of organic TRU wastes will be negligible at 25°C.

(5) The gases generated by thermal degradation (70°C) were composed mainly of CO_2 (90-95 mol%) and H_2 in the case of cellulosics,[12,44] CO_2 (76 mol %), H_2, and O_2 in the case of the composite matrix, and O_2 (93 mol %) in the case of polyethylene.[11]

(6) Several experiments were conducted at LASL in order to determine the rate of thermal dewatering of sludge. Rates of dewatering at 25°, 40°, 70°, and 100°C were determined using samples of dewatered LASL process sludge (approximately 70 weight % water). Sludge samples were placed in a flowing (10 cm^3/min) nitrogen atmosphere chosen to represent conditions in which salt in a mine acts as a dessicant. It was observed that the rates of dewatering closely approximated the vapor pressures of water at the various temperatures, i.e., the time required for complete dewatering at a particular temperature, compared to the time required at 100°C, closely approximated the ratio of the vapor pressure of water at the temperature of dewatering to that at 100°C.[16] The conclusion from these experiments was that in the event of breach the sludge water will be rapidly (on a geological time scale) absorbed by salt.

Other experiments were conducted to determine the extent of salt dessication of process sludge. These experiments involved placing sludge samples in a container with reagent grade NaCl or rocksalt from the proposed WIPP location. In each case, it was found that the sludge lost 92% of the contained water (at 20° to 23°C), after which the rate of loss of additional water drastically decreased.[19] These results were interpreted to mean that the remaining 8% water is in a mildly bound form. Additional experiments ruled out attainment of equilibrium water content between the salt and sludge. Based on these results, LASL process sludge would be nearly completely dessicated by salt.

(7) Cement paste, used to immobilize certain LASL TRU waste, was found to be much more difficult to dewater than process sludge. For example, only 3.3% (w/w) of water was evolved from the paste (containing no less than 10% (w/w) water) at 100°C.[7] Some possible effects of thermal dewatering are:
   (a) Dissolution of salt to yield brine pools or lenses.
   (b) High humidity in a mine, pumped out via ventilation system during working phase of facility.
   (c) Potential enhanced corrosion of metallic waste canisters, instrumentation, and mining-engineering equipment.
   (d) Hydrolysis and hydration of minerals (anhydrite, clays, etc.) with consequent potential swelling effects.

(ε) Leaching or dissolution of waste materials resulting in the potential water/brine mobilization of radionuclides as true solutions, colloidal dispersions, or entrained particulate material.

4.3.4 Microbial Gas Generation

The existing organic unprocessed TRU wastes can serve as the energy source or nutrient for microbial growth such that different varieties of bacteria and fungi can cause significant biological degradation. The microbes in the waste are derived from humans who work with the contaminated materials and from laboratory animals, air and soil. One important consequence of the degradation is the generation of potentially explosive gas mixtures produced by various metabolic processes.[48] The status of the results from studies conducted at LASL and UNM on the bacterial degradation of organic TRU waste is presented below. The waste matrices investigated included composite, sawdust, asphalt, composite without the cellulosic content, and carboxymethyl cellulose. The sawdust is representative of the plywood used in fiberglass reinforced polyester plywood boxes (FRP) that are used for waste disposal, and the carboxymethyl cellulose is used as a medium for bacterial detection. Parameters studied for their effect on gas production, other than waste matrix, included:

(1) Incubation temperature (25°, 40°, 50°, 60°, and 70°C).

(2) Atmosphere (aerobic and anaerobic).

(3) Solution content - deionized water, WIPP brine "B" (predominantly NaCl), phosphate buffer (pH 7.0, 0.01 M), and bacterial nutrient solution (bovine serum albumin).

(4) Solution/waste ratio - "saturated," made by adding 10 ml of solution ("91 percent H_2O," brine, or nutrient) to 1 g of waste matrix; "1 percent water," made by adding 10 microliters of water to 1 g of waste, to insure that a minimum amount of water was present. This much moisture is probably present in the waste due to sorbed water or ambient humidity; and "wet," used in preliminary experiments, made by adding 1 ml of phosphate buffer to 1 g of waste.

(5) Microbial inoculant - 20 mg of soil inoculant added to 1 g of waste matrix in preliminary experiments, an equivalent amount added as a portion of the liquid in the most recent studies.

Sterilized, incubated control samples were utilized to correct for any gas generation of thermal origin. The following important observations were made for the microbial degradation experiments:

(1) Although H_2S, CH_4, O_2, NO, N_2O, and SO_2 were found in nanomolar concentrations, CO_2 was the only major gas produced in significant quantity.[49] No evolution of substantive quantities of methane was observed, although expected. It was felt that this was due to the lack of appropriate methanogenic conditions. Studies have indicated that methane would be substituted for carbon dioxide on a mole for mole basis.[50] Experiments designed to measure the rates of

methane generation from biodegradation of organic waste matrices under strict anaerobic conditions were not conducted since the program has been terminated.*

(2) Early data[51] did not clearly indicate any effect of temperature on gas generation. However, additional experiments have proved otherwise. Despite the effects of oxygen content, water, brine, and nutrient additions, increasing temperature had a positive effect on rates of microbial gas generation for the substrate asphalt, sawdust, and composite.[12,52] Also, varying the oxygen content, water concentration, nutrient level, and the addition of brine had no significant effect on rates of degradation at the levels tested (across treatments),[52] except for the case of sawdust. Here, more CO_2 appears to be generated under anaerobic conditions.

(3) Both 1% water and saturated salt brine provided enough water for biological degradation to occur. It was observed that the rates of CO_2 generation under extreme conditions (high temperature, high salt, and anaerobiosis) had relatively high standard deviations. This has been interpreted to mean that a lag period is required for microbial adaptation to occur.[52] It was further stated that long term microbial enrichments under these conditions would yield organisms capable of more rapid degradation rates.

(4) Of the waste matrices studied, the largest quantities of CO_2 produced were for sawdust. When the results for the 100% sawdust were recalculated in terms of the weight percent of the cellulose in the composite matrix, the generation rates agreed fairly well with those observed for the actual composite matrix. Apparently, additional confirmatory experiments have been conducted that show the cellulosic component of the organic composite waste to be the source of most of the CO_2.[12]

(5) When plutonium contaminant was added to test specimens of organic composite waste, the rate of CO_2 evolution was drastically reduced. Contamination levels used were 2, 20, and 40 microcuries/g of waste; CO_2 generation inhibition was 53, 77, and 73%, respectively.[12] This is probably due to the toxic effects of plutonium on the microorganisms.

(6) The average rates of CO_2 production for the 72 experimental simulations conducted by UNM are given in Table 4.10. The accuracy of the data has been estimated to be ± 25%, while the precision is poor, i.e., hundreds of percent.[11] This situation did not improve for a large number of replicate experiments conducted on larger scale simulations.* The reason for this is the variability in the concentration of salt, humidity, substrates and microflora present, temperature, and inorganic nutrient availability. However, as confirmed experimentally, the

*D. E. Caldwell, University of New Mexico, private communication to G. Bida, BNL, April 16, 1981.

conditions most likely to produce microbial gas generation are the addition of brine to wastes and the storage of wastes under humid conditions.[52]

Table 4.10

Average Rates of CO_2 Generation[a] (Across Treatments)
In 72 CO_2 Simulations
(With Sterile Background Controls)
(This is Table XI of Reference 52)

Conditions	LASL Composite	Sawdust	Asphalt
25°C	5.1(3.9)[b]	9.4(6.3)	2.3(1.5)
40°C	6.5(5.8)	8.2(5.5)	0.88(0.45)
70°C	8.6(5.5)	10.4(5.5)	4.9(3.2)
aerobic	4.8(4.6)	7.3(5.1)	3.4(2.9)
anaerobic	7.4(5.8)	11.4(5.6)	2.0(1.9)
91% H_2O	4.45(3.5)	10.8(7.4)	1.0(1.0)
1% H_2O	3.8(4.7)	8.1(4.7)	2.0(2.5)
91% brine	2.9(3.0)	11.4(5.2)	2.9(3.0)
nutrient	8.9(5.3)	9.0(4.5)	3.4(3.2)

[a]Standard deviation given in parentheses.
[b]Rate of CO_2 generation given as micrograms/day/g.

Some speculations concerning microbial degradation have been made.[52] Most of the experimental simulations involved only one gram of waste. When these simulations are scaled up to the actual waste containers, the time course and magnitude of degradation may be vastly different than for the simulations. In addition, the presence of highly biodegradable materials (e.g. insects, rodents, etc.) could greatly increase the rate of gas generation from cellulosics and other organic matrices. It is anticipated that the initial linear CO_2 evolution rates should decline over a period of years due to depletion of labile organics, leaving more refractory compounds to degrade at a slower rate. It is also postulated that the rate may decline further due to possible container pressurization.

Finally, the major conclusion reached from the biodegradation studies is that microorganisms produce far more gas than that produced by physical or chemical processes.

4.3.5 Gas Generation From Chemical Degradation

Due to the long half lives of the actinides and the relatively short effective lifetime of container material, there is no incentive to design TRU waste containers that will last for hundreds or thousands of years. Waste containers are useful in waste processing, temporary storage, transportation, and

retrieval. The minimum time that a TRU waste container will be required to maintain its physical integrity will be determined by retrievability requirements. The containers that are planned for use in emplacement of TRU waste may include 210-L drums which are made of a mild steel alloy and FRP plywood boxes fitted with a steel overpack for fire protection purposes. Under certain conditions, hydrogen is generated from the corrosion of mild steel. This is the only chemical degradation mechanism of significance yielding gaseous reaction products and is of potential concern during the long term isolation phase of the repository.

The aqueous corrosion rate of mild steel is controlled by diffusion of dissolved oxygen to the steel surface, followed by cathodic reduction of oxygen:[9,10]

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

If oxygen is kept from the metal surface, the cathodic reaction is the reduction of water in neutral solution or hydrogen ions in acid solution, yielding hydrogen:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (neutral solution)} \quad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (acid solution)} \quad (3)$$

The anodic reaction is the oxidation and dissolution of iron:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (4)$$

Reaction (1) is preferred over (2) when oxygen is present and is 10 to 100 times faster.

Braithwaite measured the rate of corrosion of 1018 mild steel in inundated saturated NaCl brine at 25°C by measuring the amount of hydrogen produced or oxygen consumed.[10] His results are as follows:

(1) In aerated brine, the corrosion rate was 0.05 mm/yr and 5.4 moles of oxygen/m^2 were consumed annually.

(2) In deaerated brine, the corrosion rate was 0.003 mm/yr and 0.5 moles of hydrogen/m^2 were produced annually.

It should be noticed that these corrosion rates are similar to those observed in water only.

Another series of experiments was conducted to determine gas generation for consumption rates under more realistic, non-inundated repository environments. Rates were determined at 25°C by subjecting mild steel samples to the following conditions: (1) dry salt, (2) crushed salt with 0.5% water added, (3) crushed salt and 100% relative humidity, (4) inundated with aerated and deaerated brine, and (5) as a function of humidity. The only results we have found concerning

these experiments cover the first six months of testing. The following results were obtained:

(1) Test cells were originally filled with air to produce a realistic initial repository storage environment. The amount of H_2 produced in experiments (1), (2), (3), and (5) was negligible as expected. In less than six months, all the oxygen was consumed in experiment (3). No hydrogen production rate was reported.

(2) For non-inundated conditions, rates of oxygen consumption and corrosion were an order of magnitude or more slower than for rates found under inundated conditions. The non-inundated corrosion rates decreased as the relative humidity decreased from 100 to 32%.

(3) The effect of salt in low moisture environments was insignificant.

For corrosion under conditions of geologic isolation, the following generalizations were made concerning gas generation or consumption:[11]

(1) Any oxygen present will substantially reduce the amount of hydrogen produced.

(2) Under aerated conditions, corrosion reactions will result in a net decrease in the total number of moles of gas present due to oxygen consumption.

(3) Overall, if the oxygen is depleted and water is present, a total of 672 moles of H_2 can theoretically be produced from the complete corrosion of a 210-L drum, at a maximum rate (at 25°C) of two moles/yr. A 210-L drum has a total surface area of 4 m^2. This estimate assumed no protective coating on the drum (such as paint), a constant corrosion rate, and a constant supply of oxygen.

(4) No hydrogen will be produced if moisture does not contact the steel drum (dry salt); the only reaction, which will be extremely slow, is:

$$4Fe + 3\ O_2 \rightarrow 2Fe_2O_3 \qquad (5)$$

As a final note, protective coatings on steel containers have been shown to significantly reduce corrosion rates under a variety of conditions.[12] The following materials, in decreasing order of durability, were tested:

Coal Tar Epoxy > Polyamide Epoxy > Chlorinated Rubber
Acrylic Enamel >> Lacquer.

4.3.6 Comparison of Degradation Mechanisms

For the purposes of this Final Report, this completes the discussion of the DOE program conducted to determine the potential for gas production due to various degradation mechanisms and the potential consequences of this production

during the operational phase of a repository. As was briefly mentioned in the Introduction (Section 4.1), waste degradation concerns during the operational phase of the repository include the combustibility of wastes or waste packaging (to be discussed in a later section), evolution of flammable, explosive, or toxic concentrations of gases, release of airborne particulate contamination, and the corrosion of waste containers which may hinder waste retrievability. The ranges of gas generation rates from degradation of some of the organic waste matrices by the various operative mechanisms are summarized in Table 4.11. The rates neglect factors that may tend to decrease the rates, e.g., pressure, matrix depletion, unfavorable geochemical environment, etc. Gas generation rates due to different mechanisms are not additive; the resultant (non-gas) degradation products from one mechanism, e.g., radiolysis or thermal, may not be optimal starting materials for another mechanism, e.g., bacterial. However, multiple modes of degradation can proceed simultaneously. The major gases produced by degradation of various organic matrices are summarized in Table 4.12.

The concern about gas generation stems from the possible consequences for the performance objectives of the repository, namely, safety during the operational phase and radionuclide containment during the long term isolation phase. Among the consequences of gas generation that are important in view of the results discussed above are pressurization of the waste container and the combustion/explosion hazards of the gases produced. In 1970, the AEC issued a directive dealing with the continued burial of TRU wastes.[40] The directive also called for packaging and storing conditions that would allow retrieval for a period of twenty years. Thus, much of the work on gas generation via degradation of TRU wastes is concerned with the behavior of the waste presently buried and stored in steel drums or FRP boxes. It is also for this reason that Molecke[11] chose to express gas generation rates in terms of characteristics that are typical of existing TRU wastes. In the absence of waste form and canister requirements for this waste, the characteristics listed in Table 4.2 and the parameters described above provide a convenient reference scenario for the estimation of probable gas generation ranges. Based on some of the experimental data presented, the total amounts of gas generated per year per drum of existing and developmental TRU waste matrices have been estimated for each degradation mechanism considered.[12] These estimates, summarized in Table 4.13, represent the most probable ranges anticipated along with upper and lower limits that reflect the uncertainties in the measured data. We note that some of the data listed in Table 4.13 are not the same as those given in Table 4.11. The reason for this is that more recent data than those given in Reference 12 were available to us. However, we chose to use the information from Reference 12 since it was not clear to us how some of the experimental uncertainties in the data were estimated. Regardless, it is important to note the rather large uncertainties associated with some of the data. Based on the experimental data accumulated, a rank ordering has been made of the relative quantities of gas generated by an individual mechanism for existing TRU contaminated wastes under a given set of environmental conditions for bedded rocksalt.[11,12]

(1) Microbial (greatest potential, but largest inherent uncertainty).
(2) Thermal (70°C, probably insignificant at 25°C).
(3) Radiolytic.
(4) Corrosion (dry, aerobic conditions).

Table 4.11

Observed Ranges of Initial Gas Generation Rates
(Some of these data were taken from Table 13 of Reference 11)

Mechanism	Matrix	Total Gas Rate (moles/year/container)		Comments
Radiolysis	Cellulosics	0.0073		LASL, SRL
	Polyethylene	0.010-0.012		LASL
	PVC	0.0039-0.039		LASL
	Composite	0.0054		LASL
	Process Sludge	0.70		6.9 Ci
	Concrete-TRU Ash	0.046-0.98		poured, 15 Ci (SRL)
	Concrete-TRU Ash	0.00045-0.046		heated, 15 Ci (SRL)
	Asphalt	1.1		7.7 Ci
	Contaminated Soil	6.8		11.5 Ci (RHO)
Thermal	Paper	1.5		70°C
	Polyethylene	1.9		70°C
	Composite	0.02-0.20		40°C, calc.
		Aerobic	Anaerobic	
Bacterial	Composite	1.6-3.1	2.3-4.9	25°C
		1.3-5.4	0-7.8	40°, 70°C
	Plywood Box	0-16	11-26	25°C
		2.8-18	4.7-24	40°, 70°C
	Asphalt	0-3.7	0-4.8	25°C
		0-9.3	0-6.7	40°, 70°C
Corrosion	Mild Steel	2.0		wet, deaerated
Alpha Decay	He Generation	3.7×10^{-8}		0.039 Ci
		1.5×10^{-5}		15 Ci

Table 4.12

Major Gases Produced From Degradation of Organic Waste Matrices

Mechanism	Matrix	Gas(es) Produced
Radiolysis	Cellulose	H_2, CO, CO_2
	Polyethylene	H_2
	PVC	H_2, CO, CO_2, CH_4
	Composite	H_2, CO_2
	Asphalt	H_2, CH_4
	Concrete-TRU Ash	H_2, O_2
	Contaminated Soil	N_2, O_2, H_2, CO_2
Thermal	Cellulose	CO_2, H_2
	Composite	CO_2, H_2, O_2
	Polyethylene	O_2
Microbial	Cellulose	CO_2
	Composite	CO_2
	Asphalt	CO_2
Corrosion	Mild Steel	H_2 (anoxic, wet environment)

Table 4.13

Summary of TRU Waste Degradation Rates
(This is Table III of Reference 12)

Mechanism/Matrix	Gas Generation Rate[a] (Moles/Year/Drum)[b]	Comments
Microbial		
Composite, Aerobic	0-(1.3-5.4)-8	
Composite, Anaerobic	1-(2.4-7.9)-12	
Plywood Box, Aerobic	0-(0.5-2.9)-4	
Plywood Box, Anaerobic	0.4-(0.8-4.2)-6	
Bitumen, Aerobic	0-(0.1-3.4)-8	
Bitumen, Anaerobic	0-(0.6-4.8)-7	
Thermal Decomposition		
Cellulosic (Paper)	0.7-(1.3)-2	(70°C)
Organic Composite	0-(0.02-0.2)-0.4	(40°C, calculated)
Alpha Radiolysis		
Cellulosics	0.005-(0.0075)-0.011	(39 mCi)
Composite	0.004-(0.0055)-0.007	(39 mCi)
Bitumen	0.8-(1.1)-1.4	(7.7 Ci, 100 g Pu)
Concrete-TRU Ash	0.03-(0.046-0.93)-1	(15 Ci, poured)
	0.0004-(0.0005-0.034)-0.044	(15 Ci, heated)
Plutonium Contaminant	0.00002 He	(15 Ci, 200 g Pu)
Corrosion		
Mild Steel		
dry salt	0	0 micrometer/year
brine, deaerated	0-(2)-2	3 micrometer/year
brine, aerated	0	50 micrometer/year
salt, 100% humidity	0	5 micrometer/year

[a] lower limit - (most probable range) - upper limit
[b] volume = 0.21 m^3

Again, it is emphasized that the measured initial rates of gas evolution listed in Tables 4.11 and 4.13 do not take into account factors which may change the rates over a period of years and, thus, should be considered as maximum rates. The calculated total theoretical maximum number of moles of gas that could be generated if all the organic waste (60 kg) in a reference drum were degraded by a combination of improbable mechanisms is 5600.[11] However, it is estimated that the maximum number of moles of gas that could be generated under realistic conditions will be about 2000. It should be emphasized that the final total pressure in a waste container depends very much on the size of the container and its void volume (see Section 4.3.2.3). Since it is difficult to maintain a gas tight seal on the storage drums in use, the effect of gas generated in the repository has to be assessed in terms of gas accumulation/dissipation, fracture propagation resulting from stress due to pressure buildup, etc. These topics have been addressed and are discussed in the next section. The other consequence of importance, i.e., the combustion/explosion hazard of the gases, was treated in Section 4.3.2.4. Thus, the assessment of the acceptability of existing organic combustible TRU wastes for repository disposal must be made in terms of the proposed criteria that deal with both short term and long term considerations.

4.3.7 Repository Inflation Response to Gas Pressurization

The degradation of the existing TRU contaminated waste can potentially produce significant quantities of gas. Since the present waste containers are not designed to contain the gases produced via degradation, they will fill the void volumes left behind in a sealed repository. If enough gas buildup should occur in the repository, fractures could be initiated and propagated to regions where fluids are present, thus resulting in the possibility of water intrusion and leaching of radionuclides. In addition, if room closure is restricted by gas pressure, a horizontal region of higher fluid transmissivity could develop, thereby enhancing the potential for fluid motion through the repository. The assessment of the impact of gas generation has required the use of the data described above for the mathematical in-mine gas accumulation analysis. Analysis of the repository response to gas production required data on gas flow through rock salt and on the deformation of the repository rooms as a response to gas pressure. Laboratory studies of rock salt permeability have been considered along with data from borehole tests to establish a realistic data base. Also important to repository integrity considerations is the possibility of fracture initiation and propagation. The fracture toughness of representative salt core samples from waste emplacement depths was measured. Finally, to assess compression failure in the surrounding rock salt, measurement of creep rupture failure was made. These measurements were then integrated into calculations for repository response.

In the mathematical analysis of the repository inflation response, the most important part of the assessment was establishment of the effects of room closure on the surrounding medium and determination of whether the potential for fracture was sufficient to cause the integrity of the drift to be compromised (a drift is a horizontal mine passageway). The model developed for the analysis

required simultaneous solution of structural and porous flow equations developed for this study. The structural equations considered the permeation of gas through rock salt, the pressurization of the open drift, and the deformation of the surrounding rock. The results of these computations included drift closure, stress fields, and creep strains. Fracture criteria were then compared to these results to estimate the integrity of the drift. A summary of this comprehensive analysis, which was conducted by Sandia Laboratories and its subcontractors,[9] is given below. (All the technical information summarized below has been derived mainly from Reference 9. To avoid redundancy, the superscript, 9, has not been used throughout. Other references used have been noted accordingly. Although a second Sandia technical report on this subject was referred to in Reference 9, this report has not been, and reportedly will not be, issued.)

(1) Since the quantities of gas identified in previous sections could generate gas pressures on the order of the lithostatic pressure over geologic time scales, the permeability of the surrounding formation becomes an important parameter for determining if the evolved gases will be contained or dispersed. Thus, laboratory and in situ permeability measurements were conducted on rock salt. The laboratory measurements were made at various (constant) confining pressures and for differential stress states at various values of constant confining pressures in a triaxial apparatus. The observed range of permeabilities was 1 to 3.5 microdarcies, μD (a Darcy corresponds to a flow of 1 $cm^3/sec \cdot cm^2$ for a pressure gradient of 100 kPa/cm). Reduced permeabilities were observed for samples that healed after being subjected to pressures in excess of lithostatic. Since the laboratory data were obtained for carefully controlled conditions, there was some question as to the validity of these data under field conditions. Thus, in situ interval permeability tests were conducted in which 30.5-m lengths of borehole were isolated and the permeability of the surrounding formation examined. Tests were conducted at depths of 692 m and 570 m. The tests indicated that the in situ permeability for the salt layer centered at 692 m was between 12 and 21 μD. For the salt layer centered at 570 m, the permeability was approximately 3μD. It was noted that these values are not uniquely representative of the permeability for the site since the tests were conducted at only two depths in one specific borehole. Also, the radial extent tested was not characteristic of the repository dimensions. The need for more site-specific permeability data is obvious. Based on the laboratory and in situ experiments, a range of 0.050 to 5.0 μD was used in the two types of calculations performed: those in which the room volume did not change and those in which room closure and pressurization were solved simultaneously.

(2) An assessment of the fracture toughness of rock salt was made to establish the pressure needed to initiate and propagate fractures. (A material's resistance to fracture is characterizied by its fracture toughness.) Under certain laboratory conditions, rock salt exhibits

nearly linear elastic behavior for unconfined samples subjected to uniaxial tensile loading. Thus, the assessment of the fracture strength lends itself to analysis according to appropriate fracture mechanics concepts. However, for in situ loading conditions, salt exhibits a non-linear, inelastic, time dependent, stress-strain behavior under compressive stress. Experiments were conducted using halite (rock salt) and polyhalite samples from a borehole between the depths of 632 and 656 m at the WIPP site. It was observed that halite has a fracture toughness which lies on the lower end of the range of toughnesses for common rock types (e.g., limestone, granite, and tuff), while the toughness of polyhalite lies in the upper portion of this range and is approximately four times that of halite. Another fairly important observation was that the fracture toughness of halite containing a substantial amount of clay was comparable to that of clean halite. For the purpose of estimating the in situ crack initiation and propagation, it was concluded that the fracture toughness of rock salt will increase with increasing confining pressure. This conclusion was based on fracture toughness measurements on Indiana limestone. If such is the case for rock salt, then the use of the laboratory measurements are conservative for the purpose of estimating in situ crack propagation.

(3) Most of the pressure from gas generation in a gas tight repository will create a compressive loading on the rock salt surrounding the drift. This compressive loading can lead to time dependent macroscopic creep fracture. However, although the phenomenon of creep fracture is well established, there is no proven theory to predict failure. The Sandia study assumed that (a) creep fracture is the result of structural damage and that this damage can be related to the magnitude of inelastic compressive strains parallel to the greatest compressive stress, and (b) the stable time dependent strain in rock salt prior to fracture exceeds the inelastic strain. This inelastic strain is at the ultimate stress in quasi-static compression at confining pressure and ambient temperature. Thus, experimental stress-strain data at various confining pressures allowed determination of lower bound estimates of the stable time dependent strains and, in turn, an empirical expression for the strain/confining pressure limit for creep failure.

In modeling repository behavior, the magnitude of strains can be calculated as a function of stress history. Then, using the empirical strain/confining pressure limit expression for creep failure, the compressive strains can be compared with known lower bound strain/damage limits and lower bound fracture times can be estimated.

(4) For the Sandia study, a one-dimensional porous flow model was used rather than a diffusion approximation. This model assumed that only the rock directly above the storage rooms contributed to gas permeation. This assumption of one-dimensional upward flow always yields a higher pressure than actually anticipated since horizontal and downward flow are neglected.

(5) The mine design considered in the repository response calculations consisted of a number of sets of four parallel drifts 13.4 m wide and 3.66 m high separated by 10.7 m pillars. Each set of four drifts was separated from adjacent sets by 91.4 m abutments. The void fraction remaining after backfilling the stacked drums of waste was assumed to be 0.25. In order to get an upper bound on the gas pressure in a drift, the gas generation rate was assumed to be a constant 5 moles/drum/year and the total amount of gas generated was 2000 moles/drum. With the drift design given above, a total of 98.4 drums per meter of drift length was assumed.

(6) The results of the calculations for a rigid drift showed that, for the 0.5 μD case, the gas pressure that would occur with the one-dimensional porous flow model would be below lithostastic pressure (15 MPa), and it would be negligible for the 25 μD case. For the 0.05 μD case, the pressure is significantly above lithostatic such that a net expansion of the drift results.

For calculations involving simultaneous gas pressurization and room deformation, the decreasing drift volume caused the drift gas pressure to increase more rapidly than for a rigid drift. However, due to a balance between gas generation and pressure driven gas flow, the peak gas pressures were only slightly greater than for a rigid drift in the 0.5 and 25 μD cases and significantly below the rigid drift pressure for the 0.05 μD case. Important to the behavior under actual repository conditions, two-dimensional calculations indicated that the gas pressures are a factor of 1.7 lower when the entire overlying media were considered for gas permeation.

(7) Based on conventional tensile fracture criteria, the calculations predicted no repository failure. However, two additional potential failure modes were investigated: (a) macroscopic creep rupture in compression at large strains, and (b) local gas fracturing of existing cracks. For the purpose of investigating failure mode (a), the calculated drift gas pressures for a deforming room [see (6) above] and the resultant stress field-, creep strain-time histories of the repository were used in conjunction with the empirical creep fracture criterion discussed in (3) above. It was concluded that, for the 0.5 μD case, the total effective strain accumulation was within the stable creep regime and, for the 25 μD case, the possibility exists for damage in the immediate vicinity of the drifts. Due to the high confining pressures for a permeability of 0.05 μD, creep fracture is not very likely to occur.

For the purpose of assessing failure mode (b), the fracture toughness data discussed in (2) above were used in a fracture mechanics analysis derived for the problem of hydraulic fracturing of deep gas and oil wells in order to determine the conditions under which pressurized cracks will extend. The breakdown pressures at which a crack of a given length will begin to propagate were then calculated as a function of permeability. From these estimations, it was concluded that (a) the gas pressure generated in a TRU drift is of sufficient

magnitude to propagate existing fractures if the permeability is $\leq$ 0.5 μD. However, it is felt that the cracks probably would not propagate much beyond 7 to 10 m due to the steep stress gradient present around drifts, and (b) although the one-dimensional porous flow model predicts the potential for extensive crack propagation at 0.050 μD, two-dimensional modeling indicates pressures below those necessary for extensive fracture propagation.

(8) The impact of gas generation is best understood in terms of the change in drift void volume as a function of time. The drift pressure history was briefly discussed in (6) above. The results of the calculations incorporating gas pressurization and room deformation indicated that there would be no effect on the drift void volume for a permeability of 25 μD. Also, due to the high stress fields anticipated for this permeability, the calculations predicted drift closure within 200 years. For 0.50 μD, creep closure is delayed starting at 100 years after repository closure until 400 years after closure at which time gas evolution from waste degradation ceases. By 800 years, the gas pressure has dissipated and the drifts have closed. For permeabilities as low as 0.050 μD, the overburden pressure is exceeded, allowing the drift to remain open and even expand slightly.

(9) Based on consideration of the calculational results discussed in (6) through (8) above and the fracture criterion given in (3), Sandia felt that a measure of the impact of gas generation in a repository is the gas generation rate needed to reach overburden pressure of 15 MPa in a fixed volume room. Depending upon the rock salt's permeability and the gas generation rate, an equilibrium pressure can be attained in the drift before total gas generation has occurred. This equilibrium pressure can be used as an indication of the maximum pressurization of a drift independent of the total amount of gas generated. Using a two-dimensional porous flow model (peak pressures are reduced by a factor of 1.7 from the one-dimensional case), assuming a fixed volume drift, and requiring that the drift pressure not exceed lithostatic, the allowable gas generation rate was estimated to be 5 moles/drum/year for an assumed permeability of 0.10 μD. (This permeability value is conservative since it is roughly two orders of magnitude lower than the measured in situ permeabilities.) This is an interesting result since a generation rate of 5 moles/drum/year was assumed for the purpose of the repository inflation response calculations. Based on this maximum allowable gas evolution rate and the storage volume assigned to a single 210-L drum, the maximum permissible organic content of the reference waste drum for disposal in WIPP has been set at 220 kg/m^3.[47]

Evidently, mine inflation due to gas generation for the 5 moles/drum/year limit will be of no consequence as far as repository integrity is concerned. The calculations indicate that, even for the assumed case of low permeability, the only effect would be a delay in drift closure until 800 years after decommissioning, but no potential for catastrophic subsidence. As with any assessment of this nature, the accuracy of the results is in question. Sandia noted that, although their analysis was based on information from laboratory studies,

in situ experiments, etc., there is a certain amount of uncertainty inherent in all aspects of the study. For this reason, appropriately conservative assumptions had to be made. Such assumptions included one-dimensional porous flow, the in situ fracture toughness of rock salt, a constant gas generation rate, and those related to development of the creep fracture criterion. While we are aware of the recent decision to proceed with construction of the WIPP facility, for reasons related to safety and the establishment of an appropriate data base, we feel that additional considerations should be addressed and the calculations should be refined based on more site-specific information. Along these lines, we suggest that the following topics be given some consideration:

(1) Essential to generation of a realistic data base for modeling purposes is the need for more in situ data. Such needs are obvious in the areas of permeability and fracture toughness. This need is underscored since one of the attractive features of a salt repository medium is supposedly the uniformly low permeability.[6] Also, the phenomenon of creep rupture is reportedly pressure dependent and, thus, sensitive to change in porosity, permeability, and pore pressure. Only very few data appear to be available for some of these properties.[13]

(2) The repository response was modeled as a fixed volume room for one assumed gas generation rate. Given the uncertainties in the gas generation rates as discussed in Section 4.3.6, it seems worthwhile to investigate the response of the repository to a range of gas generation rates and couple this to assumed changes in drift volume. This is important since, as creep occurs, the salt permeability will increase.

(3) As discussed by Sandia, the assumptions made in proposing their creep fracture criterion were based mainly on results of fracture studies conducted on granite, sandstone, and marble. Furthermore, the criterion relied on limited data for determination of lower bound inelastic strains from quasistatic tests at ambient temperature. The proposed creep rupture criterion must be proven in full three-dimensional strain space.

(4) To our knowledge, this is the only analysis of its kind for a geologic repository. Therefore, we feel it essential that the mine inflation response be evaluated for other geomedia that are being seriously considered for waste isolation, especially if 10 CFR 60 allows the disposal of combustible waste.

While Sandia's analysis of mine inflation response seems reasonable based on the assumptions made, our critical analysis is outside of our work scope and has been limited. We feel that additional verification of the Sandia work should be carried out in the near future.

4.4 Conclusions and Assessment of Proposed NRC Criteria

The immediately applicable proposed criteria and guidelines governing the allowability of combustible organic TRU wastes in a licensed repository, as given in 10 CFR 60,[3] are as follows:

- "§60.133 Waste package and emplacement environment.

  (a) General Requirements. The Department shall insure that waste packages are designed and fabricated so that the performance objectives of §60.111 will be met. To demonstrate that the waste package meets these objectives, the Department, at a minimum, shall do the following -

  (2) Provide reasonable assurance that the in situ chemical, physical, and/or nuclear properties of the waste package and/or its interactions with the emplacement environment will not compromise the function of the waste packages. Supporting analyses shall include, but not be limited to, evaluation of the following factors: Solubility, oxidation/reduction reactions, corrosion, gas generation, thermal effects, mechanical strength, mechanical stresses, radiolysis, radiation damage, nuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

  (3) Provide reasonable assurance that the in situ chemical, physical, and/or nuclear properties of the waste package and/or its interactions with the emplacement environment will not compromise the function of the site or engineered elements of the geologic repository. The supporting analyses shall include, but not be limited to, evaluation of the following factors: Solubility, oxidation/reduction reactions, corrosion, gas generation, thermal effects, mechanical strength, stress, radiolysis, radiation damage, nuclide retardation, leaching, fire and explosion hazards, thermal loads, and synergistic interactions.

- "§60.133
  (b) Waste Form Requirements. The Department shall accept waste for disposal only if it meets the following criteria -

  (4) Combustibles. All combustible radioactive wastes must have been reduced to a noncombustible form unless the associated packaging is such that a fire involving a single package will not -

  (i) Compromise the integrity of other packages;
  (ii) Result in radiation exposures or releases of radioactive materials in excess of permissible levels, and
  (iii) Adversely affect any safety related structures, systems, or components.

(5) Explosive, pyrophoric, and toxic materials. The Department shall insure that there are not explosive or pyrophoric materials in the radioactive waste, nor are there chemically toxic wastes that could compromise either the operation or performance of the repository or adversely affect operator safety."

In addition, the radionuclide release rate criterion of one part in 10^5/yr of the TRU activity present at the time of decommissioning that we have adopted for the purpose of TRU waste form evaluation must be considered. For comparison, the Waste Acceptance Criteria that have been formulated as a result of the WIPP TRU Waste Experimental Characterization Program are summarized in Table 4.14.[9,47]

In formulating our recommendations concerning the allowability of organic combustible TRU waste in a licensed repository, the following arguments and conclusions from the available data have been considered with respect to the criteria given above:

(1) Unquestionably, existing TRU waste has not been shown to conform with the radionuclide release rate criterion of 10^{-5}/yr. Although leaching experiments are reportedly planned for combustible and non-combustible TRU waste as part of an in situ experimental program,[13] meaningful results will be difficult to obtain because of anticipated experimental problems and interpretation of the data associated with leaching a drum or plywood box of simulated or actual combustible waste. In addition, intercomparison of data with those for developmental waste forms according to some standardized methodology (e.g., MCC tests) will be nearly impossible because of a lack of uniform parameters such as surface area, surface area to solution volume ratio, nonuniform leachant flow rate (in the case of existing TRU waste), etc.

(2) Although much useful information has been accumulated, large uncertainties and discrepancies in some of the experimental work necessitate that the results be viewed with caution. These discrepancies for the thermal and radiolytic degradation of organic wastes have been identified in Sections 4.3.2.1, 4.3.2.2., and 4.3.3 above, and elsewhere.[53] Also, as noted in section 4.3.6, large uncertainties exist in the experimental data and, hence, the gas generation rates. For example, the experimental uncertainty (precision) in the rates of CO_2 production from microbial degradation is reportedly some few hundred percent.

(3) It appears that bacterial degradation has the potential to generate the largest amount of combustible gas under methanogenic conditions. As discussed in Section 4.3.4, it has yet to be shown experimentally that methane will be generated under anaerobic conditions. Regardless, large quantities of gas are expected from the biodegradation of cellulose (waste plus FRP plywood boxes), even under aerobic conditions. Additional important information is lacking in this area, e.g., gas generation as a function of time (for both rate and quanti-

Table 4.14

WIPP Waste Acceptance Criteria for Contact Handled and Remotely Handled TRU Waste
(Taken from Table 5-1 of Reference 13)

Criterion	WASTE FORM	
	Contact Handled TRU Waste	Remotely Handled TRU Waste
Combustibility	No limit, must be packaged in steel containers or overpack.	Same as for contact handled TRU waste.
Gas generation	Gas generation by all mechanisms must not exceed 10 moles/m^3 of disposal-room volume per year under repository conditions. In terms of waste composition, this criterion may be interpreted to mean that the average organic content of contact handled TRU waste may not exceed 14 lb/ft^3 for waste in 55-gallon drums and 6 lb/ft^3 for waste in other containers.	No criterion; quantities are insignificant
Immobilization	Powders, ashes, etc. must be bound in glass, concrete, ceramic, or other approved matrix; free liquids are not allowed.	Same as for contact handled TRU waste.
Explosives	Not allowed.	Same as for contact handled TRU waste.
Pyrophorics	Small quantities (up to 1% of the waste by weight) of radionuclide-metal pyrophorics may be accepted with other waste forms if they are dispersed throughout the waste.	Same as for contact handled TRU waste.
Toxic and corrosive materials	Toxic materials allowed only with special materials procedures and precautions; corrosive materials will not be accepted.	Same as for contact handled TRU waste.
Sludges and free liquids	Sludges and other waste forms containing readily desorbable water under repository conditions will not be accepted.	Same as for contact handled TRU waste.

ties of gas produced) and the effect of pressure on generation rates. Another possible consequence of the nutrient rich environment provided by organic waste is the generation of chelates by heterotrophic microorganisms. It has been shown that PuO_2 can be dissolved by a compound that is representative of naturally occurring cation binding agents.[52] This can result in enhanced radionuclide mobility. It has been speculated that the presence of highly biodegradable materials which may occur in waste packages could greatly increase the rate of gas generation from cellulosics and other organic matrices. Finally, the potential for gas generation depends on the proper type and quantity of bacteria and how well they fluorish in a repository environment. This behavior will be difficult, if not impossible, to predict.

(4) It has been stated[14] that drums containing the average amount of Pu-239 contaminated organic wastes do not generate measurable quantities of gas and, indeed, data accumulated over a two year period for drums with low Pu-239 loadings support this conclusion. However, it is possible that given sufficient accumulation of total dose, presence of oxygen, and the uncertainty in some of the data, explosive mixtures of hydrogen and oxygen are attainable in some of the drums. If the generation of gas is independent of dose rate and decreases slowly with time at low Pu loadings, then measurable quantities of gas could indeed be generated in due time. It should be noted that an estimate of the amount of H_2 produced (extrapolated to 20 years) from radiolysis of Pu-239 contaminated combustible organic material[17] would exceed explosive limits in air in a closed storage facility.[14]

(5) One of the most important observations of the degradation of cellulosic material was the presence of a tan powder in the test cylinders that were opened after termination of the radiolysis experiments.[14] This powder was found to contain about 50% of the TRU contaminant originally added. It was also highly combustible and easily dispersible.

(6) The enhancement of radiolytic gas generation rates by increased temperatures will serve to generate explosive gas mixtures over relatively shorter time periods. Should TRU waste be placed in the same repository as HLW, this synergistic effect[16] will persist for some time since the repository temperature will rise fairly rapidly (e.g., to about 50°C for one scenario[11]) and then return to ambient very slowly.

(7) An argument has been made that the rate of radiolytic degradation of cellulose will decrease as the container pressure increases and, thus, there will be an upper limit to the amount of gas generated. The fact that the steel drums (and FRP boxes) presently in temporary storage leak at pressures in slight excess of one atmosphere precludes any potential benefit of pressurization. This is a moot point until the discrepancy in the results for the high pressure versus self-pressurization experiments is clarified (see Section 4.3.2.1 above).

(8) Radiolysis can and does produce combustible and explosive gas mixtures in drums of trench stored, highly Pu-238 contaminated TRU wastes. Caution has been suggested in attempts to recover or reprocess temporarily stored Pu-238 contaminated wastes due to the potentially explosive atmospheres within these drums. This same warning was issued for the Pu-239 contaminated wastes that have been in storage the longest.

(9) The amount of combustible TRU contaminated waste in retrievable storage at LASL, for example, is about 20% (v/v) of the total inventory. However, only a few items, combustible and non-combustible, do not have the potential to be gas generators. In a study aimed at establishing parameters for predicting explosiveness under a variety of conditions, 50% of the organic waste matrices studied generated explosive atmospheres.[14] The initial gas samples were collected after only 94 days of storage.

(10) Cast concrete may yield appreciable quantities of gas (and pressure in a sealed container), mainly hydrogen, under alpha radiolytic conditions over long periods of geologic isolation. Although the radiolytic reduction of water in concrete is similar to that of liquid water, the concrete-TRU ash system is sufficiently complicated such that the mechanism of alpha radiolysis is not completely understood. Since the methods used to reduce the quantities of gas generated from the concrete are readily available, effective, and cheap, it seems prudent to make use of them to reduce the hazards due to possible container pressurization and/or explosion of the evolved gas(es).

(11) It has been noted that the radioisotopic composition of contact handled TRU waste varies widely among the DOE facilities that generate the waste.[11,13] This is also true of the organic matrix content. Because of this variability in waste composition, the rates at which degradation will take place and gases will be generated will be highly variable. Also, it is very difficult to assay a container of existing organic combustible waste for radionuclide content.[54,55] Thus, not only will it be difficult to show that a container of waste should or should not be classified as TRU waste, due to the heterogeneous nature of typical TRU waste, it will be difficult (and probably costly) for a license applicant to demonstrate compliance with a gas generation criterion, should one be imposed.

(12) Sandia Laboratories conducted several tests to determine the extent to which FRP plywood boxes and 210-L steel drums act as barriers to the prevention of fires that could involve the contained waste under credible fire scenarios. The major conclusions of this study were:

(a) Plywood boxes failed to function as effective fire barriers for contained waste when exposed to fire. In addition, they added fuel to the fire.

(b) Drums of 210-L capacity were susceptible to failure due to internal pressure buildup and loss of container lids. Some of the contained waste was scattered about the fire test area and the rest was exposed to open flames.

(c) For each type of container, fire was capable of propagating through a stack of the containers.

(d) Tests of both boxes and drums have shown that very rapid response will be required to prevent breaching of containers and consequent contamination.

Measures recommended by Sandia to reduce the potential container fire hazard included steel overpacks for both plywood boxes and drums (six per overpack), automatic fire detection and suppression systems, and portable systems for use at the open face of the storage stacks. The metal overpacks, however, will have to be vented to prevent bulging (with resultant stack instability) and to insure the integrity of the metal fire barrier. Use of metal overpacks in conjunction with inorganic insulation around the waste containers has not yet been demonstrated in actual fire tests.[9]

(13) Processing of combustible organic TRU wastes followed by immobilization could lead to the elimination or substantial reduction of gas production by bacterial, thermal, and radiolytic processes. Results on immobilization of TRU incinerator ash in concrete (SRL and MF) are encouraging. Also, studies on alpha radiolysis of borosilicate glass have detected no gaseous products.[56] The benefits of processing also include volume reduction plus greater acceptability for purposes of handling, transportation, and mine emplacement.

4.5 Recommendations

Based on the currently available information we have evaluated regarding the potential for the evolution of toxic and/or explosive atmospheres within the waste package or emplacement room, we strongly recommend that combustible organic TRU waste be processed (by incineration, slagging, etc.) and the residue be immobilized in an inert, durable waste form for the purpose of long term repository isolation. The key reasons for suggesting this recommendation are:

(1) The existing TRU waste has not been shown to meet the 10^{-5}/yr release rate criterion adopted for the purpose of this report. From an experimental point of view, we feel that, for non-processed waste, it will be difficult, albeit impossible, to show compliance with this criterion.

(2) Ease of conformity with other existing proposed criteria.

(3) Ease of assaying for TRU radionuclide content.

(4) Facilitation of waste handling at the repository.

(5) Processing of the waste will provide greater assurance of both short term and long term safety.

(6) Elimination of the potential for fire or explosion (with subsequent dispersion of radionuclides) in a handling, transportation, or emplacement accident due to combustion of the organic waste itself, the FRP plywood boxes, or due to combustion or explosion of the gases accumulated in the waste containers.

(7) Elimination or reduction of gas generation via the degradation mechanisms discussed.

(8) The volume reduction accomplished at the same time.

As a follow-up to (6) above, we further recommend that the "Combustibles" subsection of 10 CFR 60 [§60.133(b)(4)] be rewritten so as to require exclusion of combustible radioactive wastes from repositories. As this section is written "...unless the associated packaging is such that a fire involving a single package will not (i) compromise the integrity of other packages," this condition can be construed to mean that as long as a fire involving a single package does not spread to, or, more accurately, "compromise the integrity of," other packages, then the burning of isolated packages is acceptable in terms of not violating any regulations. Thus, a whole repository could be allowed to be engulfed as long as each fire was isolated within some package boundary and the consequences of these individual fires did not affect anything but the package that was destroyed. Furthermore, compliance with §60.133(b)(4)(ii) and (iii) after single package fire may be difficult to satisfactorily demonstrate for licensing purposes. These problems, and others discussed above, are essentially eliminated by requiring processing of the combustible wastes prior to disposal.

Finally, there is some concurrence within DOE for our recommendation. In their most recent strategy document for the TRU Waste Management Program,[57] DOE states "...that most combustible waste will not meet repository acceptance criteria." At that time,[57] DOE strategy concerning TRU waste called for incineration of newly generated, retrievably stored, and possibly some buried TRU combustible trash. As stated in Reference 57, "The primary goal of incineration is volume reduction, but it can also result in weight reduction, the elimination of flammability and gas generation hazards, and preparation for subsequent immobilization."

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5. CONCLUSIONS AND RECOMMENDATIONS

The task on Alternative TRU Technologies addresses several areas of concern to NRC's licensing requirements set forth in the Federal Register version of 10 CFR 60, particularly Sections 60.111, Performance Objectives, and 60.133, Waste Package and Emplacement Environment. Certain conclusions have been drawn and recommendations made in the body of the report. These are assembled in this section along with a discussion of other points specified in the current task. The conclusions and recommendations are based on the relevant information generated by the DOE waste management program and certain foreign projects up to the end of 1980.

5.1 Allowability of Combustible Waste in the Repository

Based on the overwhelming evidence and arguments in favor of processing (see Sections 4.4 and 4.5), the recommendation is made that combustible organic TRU waste not be allowed in geologic repositories. Since incineration and acid digestion are well established technologies, we feel the position should be taken that all organic TRU waste be processed and the product immobilized in a suitable waste form before emplacement. Further support of this position is obtained from volume reduction considerations, covered in the next Section (5.2.1). It is our feeling that it will be easier to meet proposed requirements by processing plus immobilization in an appropriate matrix than by attempting to prove that the thermal, chemical, and radiological stability of the combustible trash (and its associated packaging) (1) will not affect radionuclide containment and/or migration, and (2) will not affect (or be affected by) the emplacement medium. Because of the compelling nature of the arguments presented, the processing technologies available, and the level of research effort required to show that combustible TRU waste complies with NRC regulations, we have not made any research recommendations concerning informational shortcomings of the data base for gas generation from alpha-contaminated organic waste. We wish to make the point that the informational shortcomings are in the data base for demonstration of compliance of organic combustible TRU waste with NRC regulations and have no bearing on the disposal of combustible TRU waste in the WIPP facility.

5.2 Waste Volume Reduction

5.2.1 Combustible Wastes

The recommendation has already been made that combustible organic TRU wastes not be allowed in federal repositories because of the problems associated with gas generation. Even if it were permissible, there is still an important radiological incentive to keep the volume of waste to a minimum so as to decrease both handling and transportation requirements and thereby reduce risk to the work force and to the public. Volume reduction can readily be achieved by incineration or acid digestion, and immobilization of the residue in a suitable waste form. Besides possessing benefits (e.g. economic) that accrue from volume reduction for its own sake, such treatment has the advantages already mentioned of minimizing the potential for gas generation and decreasing the probability of radionuclide release.

5.2.2 Contaminated Metal

A large fraction of the total TRU waste comes from contaminated metal. Ferrous metals from failed and decommissioned equipment make up the bulk of this waste at the present time, but Zircaloy cladding hulls will contribute substantially if processing of LWR fuel becomes a standard part of the commercial fuel cycle. As described in Section 3.5, methods for decontaminating both classes of metallic waste are well enough in hand that they could presumably be developed to full engineering scale in a short time. Reduction of contamination levels to well below the TRU limit of 10 nCi/g is routinely achieved, permitting the material to be disposed of as LLW. The volume of secondary waste has, in almost all cases, been shown to be a relatively small fraction of the original metal volume. Thus, the methods to obtain appreciable reduction in the volume of waste for geologic disposal are available. There is the same radiological incentive for achieving reduction in the volume for geologic disposal here as with combustible organic waste (Section 5.2.1), namely reduction of risk through decreased handling and transportation requirements.

5.3 Criteria for Acceptance of Metallic Waste

The philosophy behind DOE's decontamination strategy, as described above and in Section 3.5, is laudable and should certainly be put into practice. However, it would appear that NRC could not justify requiring DOE to implement it on the basis of volume reduction alone, even with the probable associated decrease in risk.

There is nothing in the Federal Register version of 10 CFR 60 which would prevent metallic TRU wastes from being accepted in a geologic repository. The only requirement which might exclude it is Section 60.111(c)(3)(ii) which limits the TRU release rate from the engineered system. With most TRU metallic waste, the contamination is on the surface. Thus, in a repository, after occurrence of the expected conditions of flooding and containment breaching, the TRU contamination would very quickly be subject to removal, or release, from the metal. Depending on its chemical and physical form (soluble compound, relatively insoluble oxide, colloidal dispersion, etc.) the release rate from the engineered system could potentially be very much higher than 10^{-5} per year. We consider that it would be very difficult for DOE to guarantee the chemical and physical form of the TRU activity under these circumstances, and it would seem logical for it instead to implement its decontamination strategy so that the metallic waste could be treated as LLW. However, if DOE did not do this, NRC presumably should not specifically require decontamination but could simply rule on the basis of the release rate criterion of Section 60.111(c)(3)(ii).

5.4 Emplacement of TRU Waste and HLW in the Same Repository

The possibility of disposing of HLW and TRU waste packages in close proximity to one another on the same horizon in a licensed repository brings up the question of compatibility of TRU waste and HLW in the same repository.

The matter can be considered from two points of view, namely that of how TRU waste could affect emplaced HLW and/or the repository, and that of possible effects of HLW on emplaced TRU waste.

5.4.1 Possible Problems Caused by TRU Waste

The most obvious problem which could arise from TRU waste is that of gas generation from combustible waste and cerain waste forms. Release of toxic, combustible, or explosive gases would constitute a hazard to personnel, and posssibly to waste packages, during repository operations. After the repository closure, combustible or explosive gases could cause damage to the repository and waste packages. Such problems would be greatly reduced if waste forms generating gases were excluded from the repository.

A possibility also exists of generating hydrogen and oxygen from α-radiolysis of water if TRU waste containers were breached and actinides leached out of the TRU waste form into ground water in the repository. However, if ground water were in the repository, it would be subject to intense gamma radiolysis from the HLW waste packages. Thus, for hundreds of years, gas generation from this source would be considerably greater than that from α-radiolysis even if all the TRU activity were released from the TRU waste packages, so that the contribution to this problem from TRU waste would be small.

5.4.2 Effects of HLW on TRU Waste

The principal way in which HLW would affect TRU waste emplaced in the same repository is through the increase in temperature which would occur over the first one or two hundred years and which could cause accelerated degradation of the TRU waste form. However, according to conceptual repository designs, TRU waste and HLW are to be located on different levels of the repository and at a reasonable distance apart, so the temperature rise in the TRU waste would be small, and so would any problem related thereto. The packaging for the TRU waste is not required to avoid container breaching for any length of time after repository closure. Thus the only precaution to be observed for TRU waste is to have a waste form which will satisfy criteria at the higher temperature caused by the HLW, as well as the 30-40°C expected for TRU waste by itself after the thermal pulse has passed.

5.5 Combination of HLW and TRU Waste

Section 2.10 contains a detailed discussion of the work which has been done on combining TRU waste and HLW in a glass waste form, the technical feasibility for glass and other waste forms, and the potential advantages and disadvantages of its application in the commercial sector.

Experimental work at SRL has demonstrated the feasibility of combining HLW with TRU incinerator ash alone and with a composite of incinerator ash, HEPA filter media, and electropolishing sludge, in a borosilicate glass waste form. Technical feasibility for proposed alternative waste forms seems almost certain.

The arguments for combining the two waste streams before processing into a final waste form, assuming technical feasibility, involve simplification of waste disposal procedures and reduction of the volume to be geologically emplaced. Both of these would lead to lower costs and decreased risks of exposure, because of the smaller number of immobilization facilities which would be required and the reduction in the total number of waste packages to be transported and handled (both during fabrication and at the repository).

These arguments are obvious for the case where both HLW and TRU waste are produced at the same site. Even when they are not and TRU waste would have to be shipped to an HLW immobilization facility, there could still be a net decrease in transportation over that required by separate processing. There are, on the other hand, factors which in specific instances might result in an increase in risk, or in so little benefit that the effort of combining would not be warranted. In general, however, the concept has merit and we recommend that it be employed in all appropriate situations, such as when technical feasibility can be shown and when both HLW and TRU waste are generated at the same site.

5.6 Research and Development Needed for TRU Waste Management

5.6.1 Decontamination Methods

As described in Section 3.5, while a number of processes for decontaminating facilities and equipment have been developed to a high degree of reliability in the U.S. program, management of LWR cladding hulls is in a less satisfactory state. Development work on the proposed methods was stopped before any of them could be demonstrated on an engineering scale. While the available information indicates that demonstration of one or more engineering scale process could be accomplished fairly quickly, it is deemed advisable to do the necessary development work soon so that a method will be in place for the expected advent of commercial fuel reprocessing.

The only process for decontamination of facilities and equipment in which the decontamination step itself requires more work is liquid honing. Our evaluation suggests that other methods could handle the types of jobs done by liquid honing, but, if it is felt that it should be included among those processes considered acceptable, an effective means of containing and/or collecting removed radioactive material must be developed.

5.6.2 Secondary Waste from Decontamination Processes

The secondary waste streams from most of the decontamination processes are small and suitable for waste form preparation. The information available to us indicates that this situation has not been demonstrated for the electropolishing process, although the required chemical treatments are claimed to be known. This demonstration is essential if electropolishing is to be considered completely satisfactory. Because the method is so effective as a decontamination process, we recommend that the necessary development work be carried out to ensure that the secondary waste stream can be kept small and suitable for incorporation in a satisfactory TRU waste form.

At this time, there is little or no incentive for DOE to use, or develop, high quality methods for immobilizing secondary waste from decontamination processes. However, it is probable that commercial fuel reprocessing will be commenced in the U.S. before long. When that time comes, NRC will have to re-examine the methods in use or proposed for secondary TRU waste treatment to ensure that they can satisfy licensing requirements.

5.7 Meeting the Adopted Actinide Release Rate Requirement for TRU Waste Forms

As has been stressed elsewhere in this report (see Sections 2.6.1 and 2.11), no numerical performance objective exists in 10 CFR 60 that governs TRU waste form development. The one part in 10^5/yr actinide release rate criterion in 10 CFR 60 applies to the required performance of the engineered system. Because of this fact and the requirements of NRC under this Task 2 SOW, we chose to evaluate TRU waste forms mainly on the basis of how they comply with the adopted release rate criterion of 1 part in 10^5/yr. In the discussion that follows, the conclusions we have drawn from our evaluation and the recommendations for further work that we have made were formulated within the context of this adopted criterion. It should be kept in mind that the impetus to develop a TRU waste form that meets or exceeds the 10^{-5}/yr criterion comes only from recognition that the waste form, at least for TRU, is a major barrier in the isolation and containment of radionuclides. Furthermore, the defense generated transuranic waste in this country, which is the only inventory of importance at this time, does not have to meet any of the proposed regulations discussed in this report.

Listed below in abbreviated form are the major conclusions drawn and recommendations made from our review of the literature on transuranic waste form development. Additional discussion of some of the points made below is given in Sections 2.11.1-2.11.3.

CONCLUSIONS

In addition to being conclusions, some of these points indicate areas that are obviously in need of additional effort if these waste forms are to meet the actinide release rate criterion of 10^{-5}/yr.

- An insufficient data base exists for all the TRU waste forms reviewed.

- In terms of the 10^{-5}/yr actinide release rate criterion, no TRU waste form under development has been shown to meet this requirement with any degree of confidence. In fact, the dearth of available information on the waste forms discussed leads us to conclude, at this time, that no credit can be taken by DOE for the waste form as an engineered barrier.

- In some cases, the TRU waste stream has not been adequately characterized.

- Few data are reported for waste forms containing actual waste.

- Inadequate information exists for the sensitivity of waste form properties to physical and chemical variations in the waste.

- Outside of the comparative assessment study at PNL, no standard test methods have been used in the evaluation of material properties.

- As concerns radiation damage, the available evidence indicates that effects due to alpha particle and recoil nucleus events are not expected to be a determining factor. However, this cannot be confirmed until the ranges of waste form composition and loadings are specified.

- The combination of certain TRU waste streams, e.g. incinerator ash and process sludges, with a HLW stream for processing into a single waste form appears to be a technically feasible strategy based on the available data.

RECOMMENDATIONS

The waste form-specific recommendations are too numerous and lengthy to be listed in this abbreviated section. They appear in Section 2.11.4. Instead, some generic recommendations have been listed below.

- We recommend that the following waste forms be excluded from any further serious consideration as alternative TRU waste forms: (1) the existing TRU waste inventory, (2) Urea-formaldehyde resin, (3) Bitumen, and (4) Normal cast concrete. Reasons for making this recommendation are given in Section 2.11.2.

- The extent of the solubility of various actinides in glassy and crystalline phases appears to be well known only for borosilicate glass and monazite. This parameter is important because of anticipated variations in the actinide level in some TRU waste streams.

- Data on the phase characterization and actinide partitioning in the candidate waste forms are either scarce, incomplete, or lacking altogether. In the final analysis, these data must be obtained for production prototypic radioactive waste forms. The phases identified for lab-scale samples may not necessarily be representative of those present in large scale products.

- The role of various waste stream constituents in the formation of a durable product should be elucidated. For example, see the discussion on the role that iron plays in IESB (Section 2.4.2.3).

- In the area of radiation stability:

(1) an improved understanding of the metamict state, and the metamict "transition", would increase our confidence in the isolation capabilities of crystalline TRU waste forms. Some effort should be directed toward investigating dose rate effects, and establishing the degree of equivalence between the metamict state in natural analogues and laboratory samples. Certainly, the effect of metamictization on leach behavior should be unambiguously determined.

(2) The possibility of increased radiation damage susceptibility due to alteration under the repository environment (e.g., by incongruent leaching) should be evaluated.

• There is an obvious need for actinide leach data. In this area, we recommend:

(1) use of standardized (MCC) tests with actual waste loaded samples,

(2) use of waters equilibrated with repository rock and/or potential geologic environments,

(3) that the leach mechanisms for the various waste forms be understood for long term predictive capability,

(4) thorough investigation of the possibility that actinide leach rates are solubility limited at low groundwater flow rates, and

(5) if such is the case, then the concept of valence state control of the actinides in the candidate waste form should be pursued.

While we have not outright endorsed any of the candidate waste forms based on actinide release rate, this is not to say that we feel they are incapable of meeting or exceeding the part in 10^5/yr release rate criterion. For example, the low plutonium leach rates for CPWF concrete and PNL glass 80-207 are encouraging. It should be kept in mind that many of the leach rate experiments have been conducted with samples that contain a much higher actinide loading than will be encountered in actual waste products. With some additional R & D, it is likely that some, if not all, of the candidate TRU waste forms discussed in this section will meet or exceed the release limit. We wish to emphasize one final point concerning this evaluation. The waste form is but one barrier in preventing the migration of radionuclides to the biosphere. In fact, for TRU waste, DOE has emphasized the role of both the host rock and backfill in providing efficient, cost effective redundant barriers to radionuclide migration. In addition, the chemical behavior of actinides in a geologic environment is such that the valence state and, hence, the solubility and sorption behavior can be controlled so as to minimize migration via groundwater through a repository. The objective of the engineered system, i.e., a fractional annual release, could then be met by the additional engineered barriers and would be less sensitive to the choice of waste form.

*U.S. GOVERNMENT PRINTING OFFICE : 1982 0-361-297/2007

NRC FORM 335 (7-77) U.S. NUCLEAR REGULATORY COMMISSION

BIBLIOGRAPHIC DATA SHEET

1. REPORT NUMBER (Assigned by DDC)
NUREG/CR-2333, Vol. 2
BNL-NUREG-51458

4. TITLE AND SUBTITLE (Add Volume No., if appropriate)
Nuclear Waste Management Technical Support in the Development of Nuclear Waste Form Criteria for the NRC
Task 2: Alternative TRU Technologies

2. (Leave blank)

3. RECIPIENT'S ACCESSION NO.

7. AUTHOR(S)
G. Bida and D.R. MacKenzie

5. DATE REPORT COMPLETED
MONTH September YEAR 1981

9. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)
Department of Nuclear Energy
Brookhaven National Laboratory
Upton, NY 11973

DATE REPORT ISSUED
MONTH February YEAR 1982

6. (Leave blank)

8. (Leave blank)

12. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)
Division of Waste Management
Office of Nuclear Material Safety and Safeguards
United States Nuclear Regulatory Commission
Washington, D.C. 20555

10. PROJECT/TASK/WORK UNIT NO.

11. CONTRACT NO.
NRC FIN A3158

13. TYPE OF REPORT
Final Report

PERIOD COVERED (inclusive dates)
October 1979 to May 1981

15. SUPPLEMENTARY NOTES

14. (Leave blank)

16. ABSTRACT (200 words or less)

Three main areas of transuranic (TRU) waste management are addressed: immobilization processes and waste forms for ultimate geologic disposal of TRU waste; decontamination as a method for TRU waste management; and potential problems associated with gas generation by certain TRU wastes. Waste forms are considered in terms of the regulations and criteria proposed in 10 CFR 60. Evaluation of the waste forms is based principally on ability to meet the release rate criterion of 10^{-5}/year given in the Performance Objectives of Section 111, but also on the general requirements of Section 133. The two classes of metallic waste which are candidates for decontamination treatment are Zircaloy cladding hulls from light waste reactor fuel elements, and failed facilities and equipment. Decontamination methods are addressed with regard to their ability to remove contamination to a level below the 10 nCi/g TRU limit. Other important factors are the volume reduction achieved, and compatibility of the secondary waste streams with acceptable waste forms. Gas generation by combustible TRU wastes and cast concretes containing TRU isotopes is discussed, and its potential for damage to a geologic repository is considered. Exclusion of combustible TRU waste from repositories is recommended.

17. KEY WORDS AND DOCUMENT ANALYSIS

17a. DESCRIPTORS

17b. IDENTIFIERS/OPEN-ENDED TERMS

18. AVAILABILITY STATEMENT
Unlimited

19. SECURITY CLASS (This report)
Unclassified

21. NO. OF PAGES

20. SECURITY CLASS (This page)
Unclassified

22. PRICE
$

NRC FORM 335 (7-77)